

DESCRIPTION

REFRIGERATING MACHINE OIL COMPOSITION

Technical Field

[0001] The present invention relates to a refrigerating machine oil composition.

Background Art

[0002] As the Montreal Protocol has forced manufacturers to move away from ozone layer-depleting fluorocarbons toward alternative refrigerants, refrigerating oils that are suited to use as alternative refrigerants have been studied. For instance, synthetic oils such as polyol esters and ethers that exhibit miscibility with hydrofluorocarbon (HFC) refrigerants have been known to be used as HFC refrigerant-use refrigerating oils (see the patent documents 1 to 3, for example).

[Patent document 1] Japanese Translation Publication No. H3-505602 (JP-A 3-505602) of International Publication for Patent Application

[Patent document 2] Japanese Patent Application Laid-Open No. H3-128992

[Patent document 3] Japanese Patent Application Laid-Open No. H3-200895

Disclosure of the Invention

Problems to be Solved by the Invention

[0003] However, when the above-mentioned conventional refrigerating oils that include oxygen-containing synthetic oils are used, not only is the lubricity (anti-wear property, friction property, etc.) of the refrigerating oil itself lower than those of mineral oil-based refrigerating oils, but the lubricity of the alternative refrigerants used with these is also

lower than that of ozone layer-depleting fluorocarbons, and this tends to result in lower operating stability and shorter service life in a refrigerating or air-conditioning apparatus.

[0004] Furthermore, to compensate for these drawbacks, there have been attempts at improving lubricity by improvements to the hardware of compressors and so forth, but modifications to sliding components can drive up the cost quite high, so the addition of anti-wear agents and so forth to refrigerating oils has also been studied, but satisfactory results have yet to be obtained. Also, adding a wear inhibitor or the like to a refrigerating oil can, under certain conditions, cause problems such as capillary blockage.

[0005] The present invention was conceived in light of the above problems encountered with prior art, and it is an object thereof to provide a refrigerating machine oil composition with which a high level can be attained for both lubricity and stability in a refrigerating or air conditioning apparatus in which an HFC refrigerant or the like is used, and the refrigerating or air-conditioning apparatus can be stably operated over an extended period.

Means for Solving the Problems

[0006] To solve the above problems, the present invention provides a refrigerating machine oil composition containing a polyol ester as a base oil, a phosphorothionate, a phosphorus-based additive other than said phosphorothionate, and a glycidyl ester epoxy compound.

[0007] In the description that follows, the phosphorus-based additive other than a phosphorothionate will sometimes be called simply a "phosphorus-based additive," and it shall be understood that no

phosphorothionate is included in the phosphorus-based additive.

[0008] With the refrigerating machine oil composition of the present invention, a polyol ester is used as a base oil, this is combined with a phosphorothionate and a phosphorus-based additive, and these are
5 contained along with a glycidyl ester epoxy compound, the result of which is that both lubricity and stability are sufficiently increased, so even when this composition is used along with an HFC refrigerant or the like, the refrigerating or air-conditioning apparatus can be operated stably over an extended period.

10 [0009] The increases in anti-wear property and stability provided by the refrigerating machine oil composition of the present invention are extremely useful because they can also contribute to extending the service life of a refrigerating or air-conditioning apparatus, and because of this excellent anti-wear property, the long-term reliability of a
15 refrigerating or air-conditioning apparatus can be increased even though no improvement is made to the hardware side, such as sliding components in the compressor.

[0010] Furthermore, the increases in anti-wear property and stability provided by the present invention are the result of the synergetic
20 action of a phosphorothionate, a phosphorus-based additive, and a glycidyl ester epoxy compound in a refrigerating machine oil composition in which a polyol ester serves as the base oil, and are only obtained by using these as essential components.

[0011] There are no particular restrictions on the refrigerating or
25 air-conditioning apparatus to which the refrigerating machine oil composition of the present invention is applied, but when the

refrigerating machine oil composition of the present invention is used as a refrigerating oil composition for a package air conditioner, this refrigerating oil composition preferably contains a mixed base oil of a tetraester of pentaerythritol and a fatty acid and a diester of neopentyl glycol and a fatty acid, a phosphorothionate, a phosphorus-based additive other than said phosphorothionate, and a glycidyl ester epoxy compound. The term "package air conditioner" as used in the present invention refers to a machine whose rated cooling power consumption is over 3 kW and in which the length of the piping that links the outdoor unit to the indoor unit (the piping length) is not less than 10 meters.

[0012] The air conditioners to which the refrigerating oil is applied can be classified into room air conditioners for home use, and package air conditioners typified by large, commercial-use air conditioners. These air conditioners differ not only in their output, but also in their structure. For instance, the length of the piping that links the outdoor unit with the indoor unit is short (about 5 meters) in the case of a room air conditioner, whereas the length of the piping that links the outdoor unit with the indoor unit of a package air conditioner can be as long as several dozen meters. Therefore, when a package air conditioner is used, because the piping is so long, more air and moisture can become admixed in the refrigeration cycle including the piping during installation, which can lead to the degradation of the refrigerating oil.

[0013] Also, since the refrigerating oil used in an air conditioner can be discharged from the compressor in the refrigeration cycle, the refrigerating oil needs to have characteristics that allow it to circulate through the refrigeration cycle and come back to the compressor

(hereinafter referred to as oil return characteristics). In the case of a package air conditioner, because the piping is so long, better oil return characteristics are sometimes needed.

[0014] Some of the ways for solving these problems that have been studied on the hardware side of a package air conditioner include making the deaeration conditions more stringent for the vacuum pump, or providing a dryer for removing moisture. With a refrigerating oil used in a package air conditioner, methods have also been studied for increasing the stability against air or water, and another approach has been to select a base oil that has good miscibility with refrigerants in terms of the oil return characteristics. However, with a package air conditioner in which a conventional refrigerating oil is used, a satisfactory solution to these problems has so far been elusive, in terms of both hardware and refrigerating oil.

[0015] Furthermore, a package air conditioner is the same as a room air conditioner in that there is a need for better "lubricity," such as anti-wear property, which is related to the long-term reliability of the compressor, and friction property, which are related to energy efficiency. On the hardware side, using sliding components of a higher grade has been studied, but this cannot be considered favorable because it drives up the cost. Also, the use of anti-wear agents or friction modifiers has been studied in an effort to improve the characteristics of a refrigerating oil, but a refrigerating oil having satisfactory characteristics from a practical standpoint has yet to be obtained.

[0016] In contrast, with the package air conditioner-use refrigerating machine oil composition of the present invention, a mixed

ester consisting of a tetraester of pentaerythritol and a fatty acid and a diester of neopentyl glycol and a fatty acid is used as the base oil, and this base oil is made to contain a phosphorothionate, a phosphorus-based additive other than a phosphorothionate, and a glycidyl ester epoxy compound, the result of which is that stability against air and water, miscibility with HFC refrigerants and so forth, oil return characteristics, and lubricity can all be sufficiently increased with a good balance struck between them. Therefore, with the package air conditioner-use refrigerating machine oil composition of the present invention, degradation of the refrigerating oil composition by the admixture of air or water can be prevented, adequate oil return characteristics can be ensured, wear can be prevented, and energy efficiency can be increased, and a package air conditioner can be stably operated over an extended period.

Effect of the Invention

[0017] The present invention provides a refrigerating oil composition with which a high level can be attained for both lubricity and stability in a refrigerating or air conditioning apparatus in which an HFC refrigerant or the like is used, and the refrigerating or air-conditioning apparatus can be stably operated over an extended period.

Best Mode for Carrying Out the Invention

[0018] Preferred embodiments of the present invention will now be described in detail.

[0019] Base Oil

The refrigerating machine oil composition of the present invention contains (A) a polyol ester as a base oil. A diol or a polyol having 3 to

20 hydroxyl groups, and an ester of a fatty acid with 6 to 20 carbons can be used favorably as the polyol ester.

[0020] Specific examples of diols here include ethylene glycol, 1,3-propane glycol, propylene glycol, 1,4-butanediol, 1,2-butanediol, 2-methyl-1,3-propanediol, 1,5-pentanediol, neopentyl glycol, 1,6-hexanediol, 2-ethyl-2-methyl-1,3-propanediol, 1,7-heptanediol, 2-methyl-2-propyl-1,3-propanediol, 2,2-diethyl-1,3-propanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, 1,11-undecanediol, and 1,12-dodecanediol.

[0021] Specific examples of polyols having 3 to 20 hydroxyl groups include trimethylolethane, trimethylolpropane, trimethylolbutane, di-(trimethylolpropane), tri-(trimethylolpropane), pentaerythritol, di-(pentaerythritol), tri-(pentaerythritol), glycerol, polyglycerol (2 to 20-mers of glycerol), 1,3,5-pentanetriol, sorbitol, sorbitan, sorbitol-glycerol condensate, adonitol, arabitol, xylitol, mannitol, and other polyhydric alcohols; xylose, arabinose, ribose, rhamnose, glucose, fructose, galactose, mannose, sorbose, cellobiose, maltose, isomaltose, trehalose, sucrose, raffinose, gentianose, melezitose, and other such saccharides and partial ethers of these; and methyl glucoside (oligosaccharide). Of these, preferable polyols include neopentyl glycol, trimethylolethane, trimethylolpropane, trimethylolbutane, di-(trimethylolpropane), tri-(trimethylolpropane), pentaerythritol, di-(pentaerythritol), tri-(pentaerythritol), and other such hindered alcohols.

[0022] There are no particular restrictions on the number of carbons in the fatty acid used for the polyol ester (A), but one with a

carbon number of 1 to 24 is usually used. Among fatty acids with 1 to 24 carbons, one with 3 or more carbons is preferable in terms of lubricity, with 4 or more carbons being even better, 5 or more carbons being better yet, and 10 or more carbons being particularly favorable. In terms of miscibility with a refrigerant, one with 18 or fewer carbons is preferable, with one having 12 or fewer carbons being even better, and one having nine or fewer carbons being better yet.

[0023] This fatty acid may be a linear fatty acid or a branched fatty acid, but in terms of lubricity, a linear fatty acid is preferable, and from the standpoint of hydrolysis stability, a branched fatty acid is preferable. Further, this fatty acid may be a saturated fatty acid or an unsaturated fatty acid.

[0024] Specific examples of fatty acids include pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, undecanoic acid, dodecanoic acid, tridecanoic acid, tetradecanoic acid, pentadecanoic acid, hexadecanoic acid, heptadecanoic acid, octadecanoic acid, nonadecanoic acid, icosanoic acid, and oleic acid. These fatty acids may be either a linear fatty acid or a branched fatty acid, and may also be a fatty acid in which the α carbon atom is a quaternary carbon atom (neo acid). Of these, valeric acid (n-pentanoic acid), caproic acid (n-hexanoic acid), enanthic acid (n-heptanoic acid), caprylic acid (n-octanoic acid), pelargonic acid (n-nonanoic acid), capric acid (n-decanoic acid), oleic acid (cis-9-octadecenoic acid), isopentanoic acid (3-methylbutanoic acid), 2-methylhexanoic acid, 2-ethylpentanoic acid, 2-ethylhexanoic acid, and 3,5,5-trimethylhexanoic acid can be used preferably.

[0025] As long as it has 2 or more ester groups, the polyol ester (A) pertaining to the present invention may be a partial ester in which some of the hydroxyl groups of the polyol remain unesterified, or may be a complete ester in which all of the hydroxyl groups have been esterified, or may be a mixture of a partial ester and a complete ester, but a complete ester is preferred.

[0026] There are no particular restrictions on the combination of the above-mentioned alcohol and fatty acid in the polyol ester (A) used in the present invention, but preferably a combination of the alcohol and fatty acid constituting the polyol ester (A) is selected as dictated by the required characteristics, such as lubricity, hydrolysis stability, and miscibility with HFC refrigerants.

[0027] For example, when the refrigerating machine oil composition of the present invention is used in an application in which lubricity is most important, the fatty acid composition of the polyol ester (A) is preferably not less than 20 % by mole linear fatty acid (not greater than 80 % by mole branched fatty acid), and even more preferably not less than 25 % by mole linear fatty acid (not greater than 75 % by mole branched fatty acid), and even more preferably not less than 30 % by mole linear fatty acid (not greater than 70 % by mole branched fatty acid). Examples of favorable linear fatty acids include pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, undecanoic acid, dodecanoic acid, tridecanoic acid, tetradecanoic acid, pentadecanoic acid, hexadecanoic acid, heptadecanoic acid, octadecanoic acid, nonadecanoic acid, icosanoic acid, and oleic acid. The alcohol that constitutes the polyol ester (A) is preferably a hindered

alcohol, of which pentaerythritol is particularly favorable.

[0028] When hydrolysis stability is most important, the fatty acid composition of the polyol ester (A) is preferably not greater than 20 % by mole linear fatty acid (not less than 80 % by mole branched fatty acid), and even more preferably not greater than 10 % by mole linear fatty acid (not less than 90% by mole branched fatty acid), and even more preferably not greater than 5 % by mole linear fatty acid (not less than 95 % by mole branched fatty acid), and it is particularly favorable for all of the fatty acid to be branched fatty acid. Examples of preferable branched fatty acids include 2-methylbutanoic acid, 2-methylpentanoic acid, 2-methylhexanoic acid, 2-ethylpentanoic acid, 2-methylheptanoic acid, 2-ethylhexanoic acid, 2-methyloctanoic acid, and 3,5,5-trimethylhexanoic acid. Of these, 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid are preferable, and it is particularly favorable for both 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid to be used as essential components. The mix ratio (molar ratio) of the 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid is preferably from 10:90 to 90:10, and even more preferably from 20:80 to 80:20, and even more preferably from 30:70 to 70:30. The alcohol that constitutes the polyol ester (A) is preferably a hindered alcohol, of which pentaerythritol is particularly favorable.

[0029] When miscibility is most important, it is preferable to use a mixed fatty acid consisting of pentanoic acid and/or heptanoic acid and 3,5,5-trimethylhexanoic acid, and it is particularly favorable to use a mixture of these three fatty acids. The mix ratio (molar ratio) of three different fatty acids is selected as appropriate, but the proportion of

pentanoic acid, versus the total amount of mixed fatty acid, is preferably from 1 to 60%, and more preferably 5 to 55%, and even more preferably 10 to 50%. The proportion of heptanoic acid is preferably from 1 to 60%, and more preferably 5 to 55%, and even more preferably 10 to 50%.

5 The proportion of 3,5,5-trimethylhexanoic acid is preferably not less than 10% and less than 70%, more preferably 20 to 60%, and even more preferably 30 to 50%. The alcohol is preferably one of the above-mentioned hindered alcohols, of which pentaerythritol is particularly favorable.

10 [0030] There are no particular restrictions on the pour point of the polyol ester (A) used in the present invention, but in terms of low temperature performance it is preferably not higher than -20°C , and more preferably not higher than -25°C , and even more preferably not higher than -30°C .

15 [0031] There are no particular restrictions on the acid value of the polyol ester (A), but from the standpoint of stability it is preferably 0.10 mg KOH/g or less, and more preferably 0.05 mg KOH/g or less, and even more preferably 0.03 mg KOH/g or less.

20 [0032] There are no particular restrictions on the kinematic viscosity of the polyol ester (A), but in terms of stirring resistance, the kinematic viscosity at 40°C is preferably $200\text{ mm}^2/\text{s}$ or less, and more preferably $100\text{ mm}^2/\text{s}$ or less, and even more preferably $80\text{ mm}^2/\text{s}$ or less. In terms of lubricity, the kinematic viscosity at 40°C is preferably not less than $3\text{ mm}^2/\text{s}$, and more preferably not less than $5\text{ mm}^2/\text{s}$, and even
25 more preferably not less than $10\text{ mm}^2/\text{s}$.

[0033] There are no particular restrictions on the viscosity index

of the polyol ester (A), but in terms of the stirring resistance at low temperatures, it is preferably not less than 80, and even more preferably not less than 90.

[0034] There are no particular restrictions on the amount in which the polyol ester (A) is contained in the refrigerating machine oil composition of the present invention, but from the standpoints of lubricity, stability, miscibility, and other performance aspects, this amount is preferably not less than 70 % by mass, and more preferably not less than 80 % by mass, and even more preferably not less than 90 % by mass, with not less than 95 % by mass being particular favorable, with respect to the total amount of the composition.

[0035] Further, when the refrigerating machine oil composition of the present invention is used as a package air conditioner-use refrigerating oil composition, it is preferable to use a mixed ester consisting of (A-1) a tetraester of pentaerythritol and a fatty acid (hereinafter sometimes referred to as "ester (A-1)") and (A-2) a diester of neopentyl glycol and a fatty acid (hereinafter sometimes referred to as "ester (A-2)") as the base oil. If the ester (A-1) is used alone, oil return characteristics will tend to be inadequate. On the other hand, there may be a decrease in anti-wear property if the ester (A-2) is used alone.

[0036] There are no restrictions on the number of carbons of the fatty acid constituting the ester (A-1), but a fatty acid with 1 to 24 carbons is usually used. From the standpoint of lubricity, the carbon number of the fatty acid is preferably not less than 3, and more preferably not less than 4, and even more preferably not less than 5, with

not less than 6 being particularly favorable. From the standpoint of refrigerant miscibility, the carbon number of the fatty acid is preferably 18 or less, and more preferably 12 or less, and even more preferably 9 or less.

5 [0037] The fatty acid that constitutes the ester (A-1) may be a linear fatty acid or a branched fatty acid, but a linear fatty acid is preferred from the standpoint of lubricity, while a branched fatty acid is preferred from the standpoint of hydrolysis stability. This fatty acid may be a saturated fatty acid or an unsaturated fatty acid.

10 [0038] Specific examples of the fatty acid that constitutes the ester (A-1) include pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, undecanoic acid, dodecanoic acid, tridecanoic acid, tetradecanoic acid, pentadecanoic acid, hexadecanoic acid, heptadecanoic acid, octadecanoic acid, nonadecanoic acid,
15 icosanoic acid, and oleic acid. These fatty acids may be either a linear fatty acid or a branched fatty acid, and may also be a fatty acid in which the α carbon atom is a quaternary carbon atom (neo acid). Of these, valeric acid (n-pentanoic acid), caproic acid (n-hexanoic acid), enanthic acid (n-heptanoic acid), caprylic acid (n-octanoic acid), pelargonic acid
20 (n-nonanoic acid), capric acid (n-decanoic acid), oleic acid (cis-9-octadecenoic acid), isopentanoic acid (3-methylbutanoic acid), 2-methylhexanoic acid, 2-ethylpentanoic acid, 2-ethylhexanoic acid, and 3,5,5-trimethylhexanoic acid can be used preferably.

25 [0039] The ester (A-1) may be a partial ester in which some of the four hydroxyl groups of the pentaerythritol remain unesterified, or may be a complete ester in which all of the hydroxyl groups have been

esterified, or may be a mixture of a partial ester and a complete ester, but a complete ester is preferred.

[0040] The fatty acid that constitutes the ester (A-1) may be just one of the above-mentioned fatty acids, or may be a combination of two or more of these, but the fatty acid constituting the pentaerythritol ester is preferably selected as dictated by the required characteristics, such as lubricity, hydrolysis stability, and miscibility with HFC refrigerants.

[0041] For example, when the refrigerating machine oil composition of the present invention is used in an application in which lubricity is most important, the fatty acid composition of the ester (A-1) is preferably not less than 20 % by mole linear fatty acid (not greater than 80 % by mole branched fatty acid), and even more preferably not less than 25 % by mole linear fatty acid (not greater than 75 % by mole branched fatty acid), and even more preferably not less than 30 % by mole linear fatty acid (not greater than 70 % by mole branched fatty acid). Examples of favorable linear fatty acids include pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, undecanoic acid, dodecanoic acid, tridecanoic acid, tetradecanoic acid, pentadecanoic acid, hexadecanoic acid, heptadecanoic acid, octadecanoic acid, nonadecanoic acid, icosanoic acid, and oleic acid.

[0042] When hydrolysis stability is most important, the fatty acid composition of the ester (A-1) is preferably not greater than 20 % by mole linear fatty acid (not less than 80 % by mole branched fatty acid), and even more preferably not greater than 10 % by mole linear fatty acid (not less than 90 % by mole branched fatty acid), and even more preferably not greater than 5 % by mole linear fatty acid (not less than

95 % by mole branched fatty acid), and it is particularly favorable for all of the fatty acid to be branched fatty acid. Examples of preferable branched fatty acids include 2-methylbutanoic acid, 2-methylpentanoic acid, 2-methylhexanoic acid, 2-ethylpentanoic acid, 2-methylheptanoic acid, 2-ethylhexanoic acid, 2-methyloctanoic acid, and 3,5,5-trimethylhexanoic acid. Of these, 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid are preferable, and it is particularly favorable for both 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid to be used as essential components. The mix ratio (molar ratio) of the 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid is preferably from 10:90 to 90:10, and even more preferably from 20:80 to 80:20, and even more preferably from 30:70 to 70:30.

[0043] When miscibility with HFC refrigerants and so forth is most important, it is preferable to use a mixed fatty acid consisting of pentanoic acid and/or heptanoic acid and 3,5,5-trimethylhexanoic acid, and it is particularly favorable to use a mixture of these three fatty acids. The mix ratio (molar ratio) of three different fatty acids is selected as appropriate, but the proportion of pentanoic acid, versus the total amount of mixed fatty acid, is preferably from 1 to 60%, and more preferably 5 to 55%, and even more preferably 10 to 50%. The proportion of heptanoic acid is preferably from 1 to 60%, and more preferably 5 to 55%, and even more preferably 10 to 50%. The proportion of 3,5,5-trimethylhexanoic acid is preferably 10 to 70%, more preferably 20 to 60%, and even more preferably 30 to 50%.

[0044] Three aspects were given above depending on the required characteristics, but to strike a good balance between, and achieve high

levels for, lubricity, hydrolysis stability, and miscibility with HFC refrigerants and so forth, the fatty acid composition of the ester (A-1) is preferably not greater than 20 % by mole linear fatty acid (not less than 80 % by mole branched fatty acid), and even more preferably not greater than 10 % by mole linear fatty acid (not less than 90 % by mole branched fatty acid), and even more preferably not greater than 5 % by mole linear fatty acid (not less than 95 % by mole branched fatty acid), and it is particularly favorable for all of the fatty acid to be branched fatty acid. Examples of preferable branched fatty acids include those branched fatty acids listed as examples in the description of when hydrolysis stability is most important, and it is particularly favorable for both 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid to be used as essential components. The mix ratio (molar ratio) of the 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid is preferably from 10:90 to 90:10, and even more preferably from 20:80 to 80:20, and even more preferably from 30:70 to 70:30.

[0045] There are no restrictions on the number of carbons of the fatty acid constituting the ester (A-2), but a fatty acid with 1 to 24 carbons is usually used. From the standpoint of lubricity, the carbon number of the fatty acid is preferably not less than 3, and more preferably not less than 4, and even more preferably not less than 5, with not less than 6 being particularly favorable. From the standpoint of refrigerant miscibility, the carbon number of the fatty acid is preferably 18 or less, and more preferably 12 or less, and even more preferably 9 or less.

[0046] The fatty acid that constitutes the ester (A-2) may be a

linear fatty acid or a branched fatty acid, but a linear fatty acid is preferred from the standpoint of lubricity, while a branched fatty acid is preferred from the standpoint of hydrolysis stability. This fatty acid may be a saturated fatty acid or an unsaturated fatty acid.

5 [0047] Specific examples of the fatty acid that constitutes the ester (A-2) include pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, undecanoic acid, dodecanoic acid, tridecanoic acid, tetradecanoic acid, pentadecanoic acid, hexadecanoic acid, heptadecanoic acid, octadecanoic acid, nonadecanoic acid, 10 icosanoic acid, and oleic acid. These fatty acids may be either a linear fatty acid or a branched fatty acid, and may also be a fatty acid in which the α carbon atom is a quaternary carbon atom (neo acid). Of these, valeric acid (n-pentanoic acid), caproic acid (n-hexanoic acid), enanthic acid (n-heptanoic acid), caprylic acid (n-octanoic acid), pelargonic acid (n-nonanoic acid), capric acid (n-decanoic acid), oleic acid (cis-9- 15 octadecenoic acid), isopentanoic acid (3-methylbutanoic acid), 2-methylhexanoic acid, 2-ethylpentanoic acid, 2-ethylhexanoic acid, and 3,5,5-trimethylhexanoic acid can be used preferably.

[0048] The ester (A-2) may be a partial ester in which one of the 20 two hydroxyl groups of the neopentyl glycol remain unesterified, or may be a complete ester in which all of the hydroxyl groups have been esterified, or may be a mixture of a partial ester and a complete ester, but a complete ester is preferred.

[0049] There are no particular restrictions on the combination with 25 the above-mentioned fatty acid in the neopentyl glycol ester used in the present invention, but the fatty acid constituting the neopentyl glycol

ester is preferably selected as dictated by the required characteristics, such as lubricity, hydrolysis stability, and miscibility with HFC refrigerants.

[0050] For example, when the refrigerating machine oil composition of the present invention is used in an application in which lubricity is most important, the fatty acid composition of the ester (A-2) is preferably not less than 20 % by mole linear fatty acid (not greater than 80 % by mole branched fatty acid), and even more preferably not less than 25 % by mole linear fatty acid (not greater than 75 % by mole branched fatty acid), and even more preferably not less than 30 % by mole linear fatty acid (not greater than 70 % by mole branched fatty acid). Examples of favorable linear fatty acids include pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, undecanoic acid, dodecanoic acid, tridecanoic acid, tetradecanoic acid, pentadecanoic acid, hexadecanoic acid, heptadecanoic acid, octadecanoic acid, nonadecanoic acid, icosanoic acid, and oleic acid.

[0051] When hydrolysis stability is most important, the fatty acid composition of the ester (A-2) is preferably not greater than 40 % by mole linear fatty acid (not less than 60 % by mole branched fatty acid), and even more preferably not greater than 30 % by mole linear fatty acid (not less than 70 % by mole branched fatty acid), and even more preferably not greater than 20 % by mole linear fatty acid (not less than 80 % by mole branched fatty acid), and it is particularly favorable for the fatty acid to be not greater than 10 % by mole linear fatty acid (not less than 90 % by mole branched fatty acid). Examples of preferable branched fatty acids include 2-methylbutanoic acid, 2-methylpentanoic

acid, 2-methylhexanoic acid, 2-ethylpentanoic acid, 2-methylheptanoic acid, 2-ethylhexanoic acid, 2-methyloctanoic acid, and 3,5,5-trimethylhexanoic acid. Of these, 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid are preferable, and it is particularly favorable for both 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid to be used as essential components. The mix ratio (molar ratio) of the 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid is preferably from 10:90 to 90:10, and even more preferably from 20:80 to 80:20, and even more preferably from 30:70 to 70:30.

[0052] When miscibility with HFC refrigerants and so forth is most important, it is preferable to use a mixed fatty acid consisting of pentanoic acid and/or heptanoic acid and 3,5,5-trimethylhexanoic acid, and it is particularly favorable to use a mixture of these three fatty acids. The mix ratio (molar ratio) of three different fatty acids is selected as appropriate, but the proportion of pentanoic acid, versus the total amount of mixed fatty acid, is preferably from 1 to 60%, and more preferably 5 to 55%, and even more preferably 10 to 50%. The proportion of heptanoic acid is preferably from 1 to 60%, and more preferably 5 to 55%, and even more preferably 10 to 50%. The proportion of 3,5,5-trimethylhexanoic acid is preferably 10 to 70%, more preferably 20 to 60%, and even more preferably 30 to 50%.

[0053] Three aspects were given above depending on the required characteristics, but to strike a good balance between, and achieve high levels for, lubricity, hydrolysis stability, and miscibility with HFC refrigerants and so forth, the fatty acid composition of the ester (A-2) is preferably not greater than 40 % by mole linear fatty acid (not less than

60 % by mole branched fatty acid), and even more preferably not greater than 30 % by mole linear fatty acid (not less than 70% by mole branched fatty acid), and even more preferably not greater than 20 % by mole linear fatty acid (not less than 80 % by mole branched fatty acid), and it is particularly favorable for the fatty acid to be not greater than 10 % by mole linear fatty acid (not less than 90 % by mole branched fatty acid). Examples of preferable branched fatty acids include those branched fatty acids listed as examples in the description of when hydrolysis stability is most important, with 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid being preferable, and 2-ethylhexanoic acid being particularly favorable.

[0054] The ester (A-1) and ester (A-2) may be mixed in any ratio desired in the present invention, but because the oil return characteristics will be better, it is preferable if the ester A-2 accounts for not less than 5 % by mass (not greater than 95 % by mass ester (A-1)), and more preferable if the ester A-2 accounts for not less than 10 % by mass (not greater than 90 % by mass ester (A-1)), and even more preferable if the ester A-2 accounts for not less than 15 % by mass (not greater than 85 % by mass ester (A-1)),

and even more preferable if the ester (A-2) accounts for not less than 20 % by mass (not greater than 80 % by mass ester (A-1)), and best of all if the ester A-2 accounts for not less than 25 % by mass (not greater than 75 % by mass ester (A-1)), with respect to the combined amount of the ester (A-1) and ester A-2. Meanwhile, from the standpoint of anti-wear property, it is preferable if the ester A-2 accounts for not greater than 80 % by mass (not less than 20 % by mass ester (A-1)), and more

preferable if the ester A-2 accounts for not greater than 60 % by mass (not less than 40 % by mass ester (A-1)), and even more preferable if the ester A-2 accounts for not greater than 40 % by mass (not less than 60 % by mass ester (A-1)).

5 [0055] There are no particular restrictions on the kinematic viscosity of the mixed base oil of the ester (A-1) and ester A-2, but in terms of oil return characteristics with long piping, the kinematic viscosity at 40°C is preferably 60 mm²/s or less, and more preferably 50 mm²/s or less, and even more preferably 46 mm²/s or less, with 40 mm²/s or less being particularly favorable. In terms of anti-wear property, 10 meanwhile, the kinematic viscosity at 40°C is preferably not less than 8 mm²/s, and more preferably not less than 10 mm²/s, and even more preferably not less than 15 mm²/s, with not less than 20 mm²/s being particularly favorable.

15 [0056] There are no particular restrictions on the pour point of the mixed base oil of the ester (A-1) and ester (A-2), but in terms of low temperature performance it is preferably not higher than -20°C, and more preferably not higher than -25°C, and even more preferably not higher than -30°C. There are no particular restrictions on the acid value 20 of the mixed base oil, but from the standpoint of stability it is preferably 0.10 mg KOH/g or less, and more preferably 0.05 mg KOH/g or less.

[0057] When the refrigerating machine oil composition of the present invention contains a mixed base oil of the ester (A-1) and ester (A-2), the refrigerating oil composition may further contain a polyol 25 ester other than the esters (A-1) and (A-2). Because of their excellent hydrolysis stability, esters of trimethylolethane, trimethylolpropane,

trimethylolbutane, di-(trimethylolpropane), tri-(trimethylolpropane), di-(pentaerythritol), tri-(pentaerythritol), and other such hindered alcohols are preferable as this polyol ester other than the esters (A-1) and (A-2), and esters of trimethylolethane and trimethylolpropane are particularly favorable.

[0058] Favorable examples of polyol esters other than the esters (A-1) and (A-2) include diesters, triesters, and tetraesters obtained from one or more types of fatty acid selected from among valeric acid, caproic acid, enanthic acid, caprylic acid, pelargonic acid, capric acid, oleic acid, isopentanoic acid, 2-methylhexanoic acid, 2-ethylpentanoic acid, 2-ethylhexanoic acid, and 3,5,5-trimethylhexanoic acid, and one or more types of alcohol selected from among trimethylolethane, trimethylolpropane, and trimethylolbutane, as well as mixtures of these.

[0059] It is preferable if the above-mentioned polyol ester is made up of two or more different fatty acids because this tends to improve the low temperature characteristics of the refrigerating oil composition and its miscibility with refrigerants. The concept of the polyol ester made up of two or more different fatty acids here encompasses a mixture of two or more esters of a polyol and one fatty acid, and an ester of a polyol and two or more mixed fatty acids.

[0060] To the extent that its excellent characteristics are not compromised, the refrigerating machine oil composition of the present invention may contain as a base oil an ester oil other than the polyol ester (A) (an aromatic ester, dibasic acid ester, complex ester, carbonic acid ester, etc.). It may also contain an oxygen-containing synthetic oil other than an ester oil (such as a polyvinyl ether, ketone, polyphenyl ether,

silicone, polysiloxane, or perfluoroether), mineral oil, hydrocarbon-based synthetic oil (such as an olefin polymer, naphthalene compound, or alkylbenzene), or the like.

[0061] Examples of aromatic esters include esters of monovalent to

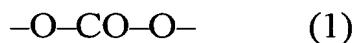
5 hexavalent, and preferably monovalent to tetravalent, and even more preferably monovalent to trivalent, aromatic carboxylic acids and aliphatic alcohols with 1 to 18, and preferably 1 to 12, carbons. Specific examples of monovalent to hexavalent aromatic carboxylic acids include benzoic acid, phthalic acid, isophthalic acid, terephthalic acid, trimellitic
10 acid, pyromellitic acid, and mixtures of these. The aliphatic alcohol with 1 to 18 carbons may be either linear or branched, and specific examples include methanol, ethanol, linear or branched propanol, linear or branched butanol, linear or branched pentanol, linear or branched hexanol, linear or branched heptanol, linear or branched octanol, linear
15 or branched nonanol, linear or branched decanol, linear or branched undecanol, linear or branched dodecanol, linear or branched tridecanol, linear or branched tetradecanol, linear or branched pentadecanol, linear or branched hexadecanol, linear or branched heptadecanol, linear or branched octadecanol, and mixtures of these.

20 [0062] Specific examples of aromatic esters obtained using the above-mentioned aromatic compounds and aliphatic alcohols include dibutyl phthalate, di(2-ethylhexyl) phthalate, dinonyl phthalate, didecyl phthalate, didodecyl phthalate, ditridecyl phthalate, tributyl trimellitate, tri(2-ethylhexyl) trimellitate, trinonyl trimellitate, tridecyl trimellitate,
25 tridodecyl trimellitate, and tritridecyl trimellitate. Naturally, when a divalent or higher aromatic carboxylic acid is used, a simple ester

composed of just one type of aliphatic alcohol may be used, or a compound ester composed of two or more types of aliphatic alcohol may be used.

[0063] Examples of dibasic acid esters that can be used to advantage include esters of a C₅ to C₁₀ linear or cyclic aliphatic dibasic acid, such as glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, 1,2-cyclohexanedicarboxylic acid, or 4-cyclohexene-1,2-dicarboxylic acid, and a linear or branched C₁ to C₁₅ monohydric alcohol, such as methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, octanol, nonanol, decanol, undecanol, dodecanol, tridecanol, tetradecanol, or pentadecanol, and mixtures of these. More specifically, examples include ditridecyl glutarate, di-2-ethylhexyl adipate, diisodecyl adipate, ditridecyl adipate, di-2-ethylhexyl sebacate, a diester of 1,2-cyclohexanedicarboxylic acid and a C₄ to C₉ monohydric alcohol, a diester of 4-cyclohexene-1,2-dicarboxylic acid and a C₄ to C₉ monohydric alcohol, and mixtures of these.

[0064] A carbonic acid ester is a compound having a carbonic acid ester bond expressed by the following formula (1) in its molecule. The number of carbonic acid ester bonds expressed by Formula (1) may be one per molecule, or may be two or more.



[0065] The alcohol that constitutes the carbonic acid ester is one of the monohydric alcohols, polyols, etc., listed as examples in the description of the dibasic acid ester and polyol ester (A) above, or can be a polyglycol or a compound obtained by adding a polyglycol to a polyol. A compound obtained from carbonic acid and a fatty acid and/or a

dibasic acid may also be used.

[0066] When an ester other than the polyol ester (A) is used, a compound with a single structure may be used alone, or a combination of two or more compounds with different structures may be used.

5 [0067] Among esters other than the polyol ester (A), dibasic acid esters and carbonic acid esters are preferable because of their excellent miscibility with refrigerants.

[0068] Among dibasic acid esters, a 1,2-cyclohexanedicarboxylic acid, 4-cyclohexene-1,2-dicarboxylic acid, or other such alicyclic dicarboxylic acid ester is preferable in terms of thermal and hydrolysis stability and miscibility with refrigerants.

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[0069] Specific examples of dibasic acid esters that can be used to advantage in the present invention include dibasic acid esters obtained from one or more monohydric alcohol selected from the group consisting of butanol, pentanol, hexanol, heptanol, octanol, and nonanol, and one or more dibasic acids selected from the group consisting of 1,2-cyclohexanedicarboxylic acid and 4-cyclohexene-1,2-dicarboxylic acid, and mixtures of these esters.

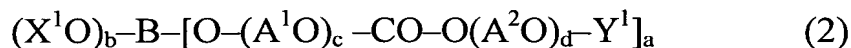
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[0070] It is preferable if the dibasic acid ester used in the present invention is made up of two or more different monohydric alcohols because this tends to improve the low temperature characteristics of the refrigerating oil composition and its miscibility with refrigerants. The concept of the dibasic acid ester made up of two or more monohydric alcohols here encompasses a mixture of two or more esters of a dibasic acid and one type of alcohol, and an ester of a dibasic acid and two or more mixed alcohols.

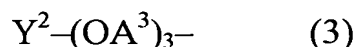
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[0071] Among carbonic acid esters, those expressed by the following general formulas (2) are preferable.



(In Formula (2), X^1 is a hydrogen atom, alkyl group, cycloalkyl group, or group having a structure expressed by the following general formula (3):



(in Formula (3), Y^2 is a hydrogen atom, alkyl group, or cycloalkyl group, A^3 is a C_2 to C_4 alkylene group, and e is an integer from 1 to 50),

A^1 and A^2 may be the same or different and are each a C_2 to C_4 alkylene group, Y^1 is a hydrogen atom, alkyl group, or cycloalkyl group, B is a residue of a compound having 3 to 20 hydroxyl groups, a is an integer from 1 to 20, b is an integer from 0 to 19, $a + b$ is an integer from 3 to 20, c is an integer from 0 to 50, and d is an integer from 1 to 50.)

[0072] In Formula (2) above, X^1 a hydrogen atom, alkyl group, cycloalkyl group, or group having a structure expressed by Formula (3). There are no particular restrictions on the carbon number of the alkyl group referred to here, but it is usually from 1 to 24, and preferably from 1 to 18, and even more preferably from 1 to 12. This alkyl group may be either linear or branched.

[0073] Specific examples of C_1 to C_{24} alkyl groups include a methyl group, ethyl group, n-propyl group, isopropyl group, n-butyl group, isobutyl group, sec-butyl group, tert-butyl group, linear or branched pentyl group, linear or branched hexyl group, linear or branched heptyl group, linear or branched octyl group, linear or branched nonyl group, linear or branched decyl group, linear or branched

undecyl group, linear or branched dodecyl group, linear or branched tridecyl group, linear or branched tetradecyl group, linear or branched pentadecyl group, linear or branched hexadecyl group, linear or branched heptadecyl group, linear or branched octadecyl group, linear or branched nonadecyl group, linear or branched eicosyl group, linear or branched heneicosyl group, linear or branched docosyl group, linear or branched tricosyl group, and linear or branched tetracosyl group.

[0074] Specific examples of cycloalkyl groups include a cyclopentyl group, cyclohexyl group, and cycloheptyl group.

[0075] Specific examples of the C_2 to C_4 alkylene group expressed by A^3 in Formula (2) include an ethylene group, propylene group, trimethylene group, butylene group, tetramethylene group, 1-methyltrimethylene group, 2-methyltrimethylene group, 1,1-dimethylethylene group, and 1,2-dimethylethylene group.

[0076] Y^2 in Formula (2) is a hydrogen atom, alkyl group, or cycloalkyl group. There are no particular restrictions on the carbon number of the alkyl group referred to here, but it is usually from 1 to 24, and preferably from 1 to 18, and even more preferably from 1 to 12. This alkyl group may be either linear or branched. Examples of C_1 to C_4 alkyl groups include the alkyl groups listed in the description of X^1 above.

[0077] Specific examples of cycloalkyl groups include a cyclopentyl group, cyclohexyl group, and cycloheptyl group.

[0078] Of the groups expressed by Y^2 , a hydrogen atom or a C_1 to C_{12} alkyl group is preferable, and a hydrogen atom or a methyl group, ethyl group, n-propyl group, isopropyl group, n-butyl group, iso-butyl

group, sec-butyl group, tert-butyl group, n-pentyl group, iso-pentyl group, neo-pentyl group, n-hexyl group, iso-hexyl group, n-heptyl group, iso-heptyl group, n-octyl group, iso-octyl group, n-nonyl group, iso-nonyl group, n-decyl group, iso-decyl group, n-undecyl group, iso-undecyl group, n-dodecyl group, or iso-dodecyl group is particularly preferable. e is an integer from 1 to 50.

[0079] The group expressed by X^1 is preferably a hydrogen atom, a C_1 to C_{12} alkyl group, or a group expressed by General Formula (3), and a hydrogen atom or a methyl group, ethyl group, n-propyl group, isopropyl group, n-butyl group, iso-butyl group, sec-butyl group, tert-butyl group, n-pentyl group, iso-pentyl group, neo-pentyl group, n-hexyl group, iso-hexyl group, n-heptyl group, iso-heptyl group, n-octyl group, iso-octyl group, n-nonyl group, iso-nonyl group, n-decyl group, iso-decyl group, n-undecyl group, iso-undecyl group, n-dodecyl group, iso-dodecyl group or a group expressed by General Formula (3) is particularly preferable.

[0080] Specific examples of compounds having 3 to 20 hydroxyl groups and in which B is a residue include the polyols listed above.

[0081] A^1 and A^2 may be the same or different and are each a C_2 to C_4 alkylene group. Specific examples of such alkylene groups include an ethylene group, propylene group, trimethylene group, butylene group, tetramethylene group, 1-methyltrimethylene group, 2-methyltrimethylene group, 1,1-dimethylethylene group, and 1,2-dimethylethylene group.

[0082] Y^1 is a hydrogen atom, alkyl group, or cycloalkyl group. There are no particular restrictions on the carbon number of the alkyl

group referred to here, but it is usually from 1 to 24, and preferably from 1 to 18, and even more preferably from 1 to 12. This alkyl group may be either linear or branched. Specific examples of C₁ to C₂₄ alkyl groups include the alkyl groups listed in the description of X¹ above.

5 [0083] Specific examples of cycloalkyl groups include a cyclopentyl group, cyclohexyl group, and cycloheptyl group.

[0084] Of these, the group expressed by Y¹ is more preferably a hydrogen atom or a C₁ to C₁₂ alkyl group, and a hydrogen atom or a methyl group, ethyl group, n-propyl group, iso-propyl group, n-butyl group, iso-butyl group, sec-butyl group, tert-butyl group, n-pentyl group, iso-pentyl group, neo-pentyl group, n-hexyl group, iso-hexyl group, n-heptyl group, iso-heptyl group, n-octyl group, iso-octyl group, n-nonyl group, iso-nonyl group, n-decyl group, iso-decyl group, n-undecyl group, iso-undecyl group, n-dodecyl group, or iso-dodecyl group is particularly preferable.

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[0085] In Formulas (2) and (3), c, d, and e indicate the degree of polymerization of the polyoxyalkylene chain, and the polyoxyalkylene chains in the molecules may be the same or different. If the carbonic acid ester expressed by Formula (2) has a plurality of different polyoxyalkylene chains, there are no particular restrictions on how the oxyalkylene groups are polymerized, which may be accomplished by random polymerization or block polymerization.

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[0086] The carbonic acid ester used in the present invention can be manufactured by any method desired, but an example is to manufacture a polyalkylene glycol polyol ether by the addition of an alkylene oxide to a polyol compound, and react this product with a chloroformate at 0 to

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30°C in the presence of sodium hydroxide, potassium hydroxide, or another such alkyl metal hydroxide, sodium methoxide, sodium ethoxide, or another such alkali metal alkoxide, or metallic sodium or another such alkali metal. Alternatively, this ester can be obtained by reacting a polyalkylene glycol polyol ether with a carbon supply source, such as a carbonic acid diester or phosgene, at 80 to 150°C in the presence of sodium hydroxide, potassium hydroxide, or another such alkyl metal hydroxide, sodium methoxide, sodium ethoxide, or another such alkali metal alkoxide, or metallic sodium or another such alkali metal. After this, the free hydroxyl groups may be etherified as needed.

[0087] The product obtained from the above raw materials may be refined to remove any by-products or unreacted components, but the presence of a small amount of by-products or unreacted components is acceptable as long as the excellent performance of the lubricating oil of the present invention is not sacrificed.

[0088] When a carbonic acid ester is used in the present invention, a compound of just one structure may be used alone, or a combination of two or more compounds of different structure may be used. There are no particular restrictions on the molecular weight of the carbonic acid ester in the present invention, but from the standpoint of improving the sealing of the compressor, a number average molecular weight of from 200 to 4000 is preferable, and 300 to 3000 is even better. The kinematic viscosity of the carbonic acid ester pertaining to the present invention at 100°C is preferably 2 to 150 mm²/s, and more preferably 4 to 100 mm²/s.

[0089] Examples of mineral oils include paraffin-based mineral oils and naphthene-based mineral oils obtained when a lubricant fraction

yielded by distilling a crude oil under normal pressure and under reduced pressure is refined by carrying out at least one of processes of solvent deasphalting, solvent extraction, hydrocracking, solvent dewaxing, catalytic dewaxing, hydrorefining, sulfuric acid washing, or clay treatment.

[0090] Of these mineral oils, the use of one that has been highly refined (hereinafter referred to as "highly refined mineral oil") is preferable because the thermal stability will be superior. Specific examples of highly refined mineral oils include refined oils obtained by subjecting a paraffin base crude oil, intermediate base crude oil, or naphthene base crude oil to normal pressure distillation, or subjecting the residue oil of normal pressure distillation to reduced pressure distillation, and then refining the resulting distillate by a standard method; deeply dewaxed oils obtained by further performing a deep dewaxing treatment after refining; and hydrotreated oils obtained by hydrotreatment.

[0091] There are no particular restrictions on the refining method in the above-mentioned refining step, and any conventional method can be used, but examples include (a) hydrotreatment, (b) dewaxing (solvent dewaxing or hydrodewaxing), (c) solvent extraction, (d) alkali washing or sulfuric acid washing, and (e) clay treatment, each of which can be performed alone, or two or more may be combined in a suitable order. It is also effective to divide up any of the above treatments (a) to (e) into a plurality of stages and perform these over and over. More specifically, examples include (i) a method in which a distillate is hydrotreated, or a method in which it is first hydrotreated and then subjected to alkali washing or sulfuric acid washing; (ii) a method in which a distillate is

hydrotreated and then dewaxed; (iii) a method in which a distillate is subjected to solvent extraction and then hydrotreated; (iv) a method in which a distillate is subjected to a two- or three-stage hydrotreatment, or then subjected to alkali washing or sulfuric acid washing; and (v) a method in which the above-mentioned treatments (i) to (iv) are performed, after which dewaxing is performed again, and this is followed by deep dewaxing.

[0092] Of the highly refined mineral oils obtained by the above refining methods, naphthene-based mineral oils, and mineral oils obtained by deep dewaxing are favorable in terms of their low temperature fluidity, because there is no wax precipitation at low temperature, and so forth. This deep dewaxing is usually accomplished by a solvent dewaxing method performed under stringent conditions, a catalytic dewaxing method involving the use of a zeolite catalyst, or the like.

[0093] The nonaromatic unsaturated component (the degree of unsaturation) of this highly refined mineral oil is preferably 10 % by mass or less, and more preferably 5 % by mass or less, and even more preferably 1 % by mass or less, with 0.1 % by mass or less being particularly favorable. Sludge will tend to be produced if the nonaromatic unsaturated component accounts for more than 10 % by mass, and as a result, there will be a tendency for blockage to occur in the expansion mechanism, such as the capillaries that make up the refrigerant circulation system.

[0094] Examples of olefin polymers include those obtained by polymerizing an olefin with 2 to 12 carbons, and those obtained by

hydrotreating a compound obtained by the above polymerization. It is preferable to use a polybutene, polyisobutene, C₅ to C₁₂ α -olefin oligomer (poly- α -olefin), ethylene-propylene copolymer, or the like, or one of these that has been hydrotreated.

5 [0095] There are no particular restrictions on the method for manufacturing the olefin polymer, which can be manufactured by any of various known methods. For instance, a poly- α -olefin can be manufactured by using an α -olefin made from ethylene as the raw material and treating this with a known polymerization method, such as a
10 Ziegler catalyst process, radical polymerization, an aluminum chloride process, or a bromine fluoride process.

[0096] There are no particular restrictions on the naphthalene compound as long as it has a naphthalene skeleton, but from the standpoint of miscibility with refrigerants, it is preferable to use one
15 which has one to four C₁ to C₈ alkyl groups and in which the total carbon number of the alkyl groups is 1 to 10, and even more preferable to use one that has from one to three C₁ to C₈ alkyl groups and in which the total carbon number of the alkyl groups is 3 to 8.

[0097] Specific examples of C₁ to C₁₀ alkyl groups had by the
20 naphthalene compound include a methyl group, ethyl group, n-propyl group, isopropyl group, linear or branched butyl group, linear or branched pentyl group, linear or branched hexyl group, linear or branched heptyl group, linear or branched octyl group, linear or branched nonyl group, and linear or branched decyl group.

25 [0098] When a naphthalene compound is used, a compound with a single structure may be used alone, or a combination of two or more

compounds with different structures may be used.

[0099] There are no particular restrictions on the method for manufacturing the naphthalene compound, which can be manufactured by any of various known methods. An example is a method in which a halide of a C₁ to C₁₀ hydrocarbon, or a C₂ to C₁₀ olefin, or a C₈ to C₁₀ styrene is added to naphthalene in the presence of sulfuric acid, phosphoric acid, silicotungstic acid, hydrofluoric acid, or another such mineral oil, acidic clay, activated clay, or another such solid acidic substance, aluminum chloride, zinc chloride, or another such metal halide (a Friedel-Crafts catalyst), or another such acid catalyst.

[0100] There are no particular restrictions on the alkylbenzene, but from the standpoint of miscibility with refrigerants, it is preferable to use one that has from one to four C₁ to C₄₀ alkyl groups and in which the total carbon number of the alkyl groups is 1 to 30, and even more preferably one that has from one to four C₁ to C₃₀ alkyl groups and in which the total carbon number of the alkyl groups is 3 to 30.

[0101] Specific examples of C₁ to C₄₀ alkyl groups had by the alkylbenzene include a methyl group, ethyl group, n-propyl group, isopropyl group, linear or branched butyl group, linear or branched pentyl group, linear or branched hexyl group, linear or branched heptyl group, linear or branched octyl group, linear or branched nonyl group, linear or branched decyl group, linear or branched undecyl group, linear or branched dodecyl group, linear or branched tridecyl group, linear or branched tetradecyl group, linear or branched pentadecyl group, linear or branched hexadecyl group, linear or branched heptadecyl group, linear or branched octadecyl group, linear or branched nonadecyl group, linear or

branched eicosyl group, linear or branched heneicosyl group, linear or
branched docosyl group, linear or branched tricosyl group, linear or
branched tetracosyl group, linear or branched pentacosyl group, linear or
branched hexacosyl group, linear or branched heptacosyl group, linear or
5 branched octacosyl group, linear or branched nonacosyl group, linear or
branched triacontyl group, linear or branched hentriacontyl group, linear
or branched dotriacontyl group, linear or branched tritriacontyl group,
linear or branched tetratriacontyl group, linear or branched
pentatriacontyl group, linear or branched hexatriacontyl group, linear or
10 branched heptatriacontyl group, linear or branched octatriacontyl group,
linear or branched nonatriacontyl group, and linear or branched
tetracontyl group (including all isomers).

[0102] This alkyl group may be either linear or branched, but from
the standpoint of suitability to the organic materials used in the
15 refrigerant circulation system, a linear alkyl group is preferable. On the
other hand, from the standpoint of refrigerant miscibility, thermal
stability, lubricity, and so forth, a branched alkyl group is preferable, and
particularly in terms of availability, a branched alkyl group derived from
an oligomer of propylene, butene, isobutylene, or another such olefin is
20 preferable.

[0103] When an alkylbenzene is used, a compound of just one
structure may be used alone, or a combination of two or more
compounds of different structure may be used.

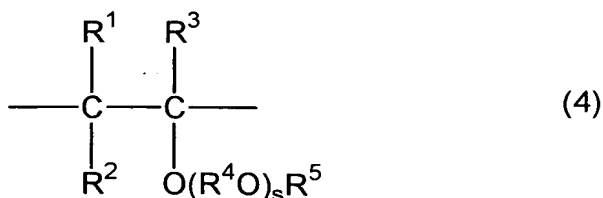
[0104] There are no restrictions whatsoever on the method for
25 manufacturing the alkylbenzene, but it can be manufactured by the
following synthesis method, for example.

[0105] Specific examples of the aromatic compounds that can serve as the raw material include benzene, toluene, xylene, ethylbenzene, methylethylbenzene, diethylbenzene, and mixtures of these. As alkylating agents, a linear or branched olefin with a carbon number of 6 to 40 and obtained by the polymerization of ethylene, propylene, butene, isobutylene, or another such lower monoolefin (preferably propylene); a linear or branched olefin with a carbon number of 6 to 40 and obtained by the pyrolysis of polyethylene, polypropylene, or the like; a linear olefin with a carbon number of 9 to 40 and obtained by separating n-paraffin from kerosene, light oil, or another such petroleum fraction and then olefinating this with a catalyst; mixtures of these; and so forth can be used as an alkylation agent.

[0106] A known alkylation catalyst can be used in the reaction of the above-mentioned aromatic compound and an alkylation agent, such as aluminum chloride, zinc chloride, or another such Friedel-Crafts catalyst, sulfuric acid, phosphoric acid, silicotungstic acid, hydrofluoric acid, activated clay, or another such acid catalyst.

[0107] Examples of polyvinyl ethers that can be used in the present invention include the polyvinyl ether compounds having structural units expressed by the following general formula (4).

[Chemical Formula 1]



(In Formula (4), R^1 to R^3 may be the same or different, and each is

a hydrogen atom or a C₁ to C₈ hydrocarbon group, R⁴ is a C₂ to C₂₀ divalent ether bonded oxygen-containing hydrocarbon group or a C₁ to C₁₀ divalent hydrocarbon group, R⁵ is a C₁ to C₂₀ hydrocarbon group, s is a number whose average value is from 0 to 10, R¹ to R⁵ may be the same or different for each structural unit, and when the structural units expressed by General Formula (4) have a plurality of R⁴O groups, the plurality of R⁴O groups may be the same or different.)

[0108] A polyvinyl ether compound composed of a random copolymer or block copolymer having structural units expressed by General Formula (4) and structural units expressed by General Formula (5) can also be used.

[Chemical Formula 2]



(In Formula (5), R⁶ to R⁹ may be the same or different, and each is a hydrogen atom or a C₁ to C₂₀ hydrocarbon group, and R⁶ to R⁹ may be the same or different for each structural unit.)

[0109] R¹ to R³ in General Formula (4) above are each a hydrogen atom or a C₁ to C₈ hydrocarbon group (preferably, a C₁ to C₄ hydrocarbon group), and may be the same as or different from each other. Specific examples of this hydrocarbon group include a methyl group, ethyl group, n-propyl group, isopropyl group, n-butyl group, isobutyl group, sec-butyl group, tert-butyl group, various pentyl groups, various hexyl groups, various heptyl groups, various octyl groups, and other such

alkyl groups; a cyclopentyl group, cyclohexyl group, various methylcyclohexyl groups, various ethylcyclohexyl groups, various dimethylcyclohexyl groups, and other such cycloalkyl groups; a phenyl group, various methylphenyl groups, various ethylphenyl groups, various dimethylphenyl groups, and other such aryl groups; and a benzyl group, various phenylethyl groups, various methylbenzyl groups, and other such arylalkyl groups. R^1 to R^3 are preferably hydrogen atoms.

[0110] R^4 in General Formula (4), meanwhile, is a C_1 to C_{10} (preferably C_2 to C_4) divalent hydrocarbon group or a C_2 to C_{20} divalent ether bonded oxygen-containing hydrocarbon group. Specific examples of C_1 to C_{10} divalent hydrocarbon groups include a methylene group, ethylene group, phenylethylene group, 1,2-propylene group, 2-phenyl-1,2-propylene group, 1,3-propylene group, various butylene groups, various pentylene groups, various hexylene groups, various heptylene groups, various octylene groups, various nonylene groups, various decylene groups, various and other such divalent aliphatic hydrocarbon groups; cyclohexane, methylcyclohexane, ethylcyclohexane, dimethylcyclohexane, propylcyclohexane, and other such alicyclic hydrocarbon groups having two bond positions on an alicyclic hydrocarbon; various phenylene groups, various methylphenylene groups, various ethylphenylene groups, various dimethylphenylene groups, various naphthylene groups, and other such divalent aromatic hydrocarbon groups; toluene, xylene, ethylbenzene, and other such alkyl aromatic hydrocarbon groups having a monovalent bond position at each of the alkyl group component and the aromatic component of an alkyl aromatic hydrocarbon; and xylene, diethylbenzene, and other such alkyl

aromatic hydrocarbon groups having a bond position at the alkyl group portion of a polyalkyl aromatic hydrocarbon. Of these, a C₂ to C₄ aliphatic hydrocarbon group is particularly favorable.

[0111] Specific favorable examples of C₂ to C₂₀ divalent ether bonded oxygen-containing hydrocarbon groups include a methoxymethylene group, methoxyethylene group, methoxymethylethylene group, 1,1-bismethoxymethylethylene group, 1,2-bismethoxymethylethylene group, ethoxymethylene group, (2-methoxyethoxy)methylethylene group, and (1-methyl-2-methoxy)methylethylene group. s in General Formula (4) is the repeat number of R⁴O, the average value of which is from 0 to 10, and preferably 0 to 5. If there are a plurality of R⁴O groups in the same structural unit, then the plurality of R⁴O groups may be the same or different.

[0112] R⁵ in General Formula (4) is a C₁ to C₂₀, and preferably C₁ to C₁₀, hydrocarbon group, and specific examples of this hydrocarbon group include a methyl group, ethyl group, n-propyl group, isopropyl group, n-butyl group, isobutyl group, sec-butyl group, tert-butyl group, various pentyl groups, various hexyl groups, various heptyl groups, various octyl groups, various nonyl groups, various decyl groups, and other such alkyl groups; a cyclopentyl group, cyclohexyl group, various methylcyclohexyl groups, various ethylcyclohexyl groups, various propylcyclohexyl groups, various dimethylcyclohexyl groups, and other such cycloalkyl groups; a phenyl group, various methylphenyl groups, various ethylphenyl groups, various dimethylphenyl groups, various propylphenyl groups, various trimethylphenyl groups, various

butylphenyl groups, various naphthyl groups, and other such aryl groups; and a benzyl group, various phenylethyl groups, various methylbenzyl groups, various phenylepropyl groups, various phenylbutyl groups, and other such arylalkyl groups. R¹ to R⁵ may be the same or different for each structural unit

[0113] If the polyvinyl ether is a homopolymer composed of just structural units expressed by General Formula (4), the carbon/oxygen molar ratio thereof is preferably within the range of 4.2 to 7.0. Moisture absorption will be excessively high if this molar ratio is less than 4.2, but miscibility with refrigerants will tend to decrease if 7.0 is exceeded.

[0114] In General Formula (5), R⁶ to R⁹ may be the same or different, and each is a hydrogen atom or a C₁ to C₂₀ hydrocarbon group. Examples of the C₁ to C₂₀ hydrocarbon group here are the same as the hydrocarbon groups listed as examples in the description of R⁵ in General Formula (4). R⁶ to R⁹ may be the same or different for each structural unit.

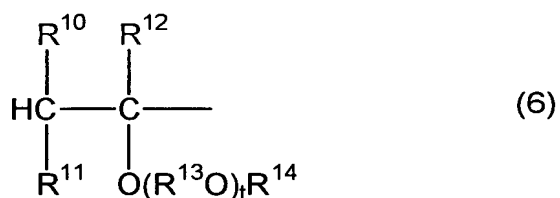
[0115] If the polyvinyl ether pertaining to the present invention is a block copolymer or random copolymer having structural units expressed by General Formula (4) and structural units expressed by General Formula (5), the carbon/oxygen molar ratio thereof is preferably within the range of 4.2 to 7.0. Moisture absorption will be excessively high if this molar ratio is less than 4.2, but miscibility with refrigerants will tend to decrease if 7.0 is exceeded.

[0116] Furthermore, in the present invention, it is possible to use a mixture of a homopolymer composed of just structural units expressed by General Formula (4), and a block copolymer or random copolymer

having structural units expressed by General Formula (4) and structural units expressed by General Formula (5). The homopolymer and copolymer here can be manufactured by polymerization of a corresponding vinyl ether monomer, and by copolymerization of a corresponding vinyl ether monomer and a corresponding hydrocarbon monomer having olefinic double bonds.

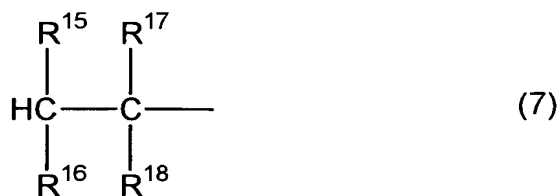
[0117] The polyvinyl ether used in the present invention is preferably one having a structure in which one of the terminal structures is expressed by the following General Formula (6) or (7) and the other is expressed by the following General Formula (8) or (9), or one having a structure in which one terminal is expressed by General Formula (6) or (7) and the other is expressed by the following General Formula (10).

[Chemical Formula 3]



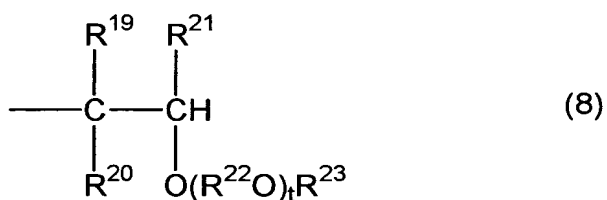
(In Formula (6), R^{10} to R^{12} may be the same or different, and each is a hydrogen atom or a C_1 to C_8 hydrocarbon group, R^{13} is a C_2 to C_{20} divalent ether bonded oxygen-containing hydrocarbon group or a C_1 to C_{10} divalent hydrocarbon group, R^{14} is a C_1 to C_{20} hydrocarbon group, t is a number whose average value is from 0 to 10, and when the terminal structures expressed by General Formula (6) have a plurality of R^{13}O groups, the plurality of R^{13}O groups may be the same or different.)

[Chemical Formula 4]



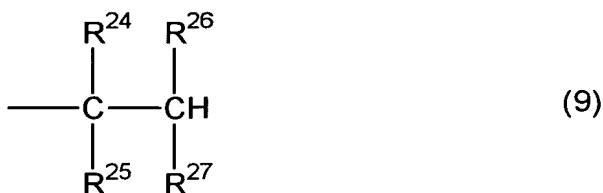
(In Formula (7), R^{15} to R^{18} may be the same or different, and each is a hydrogen atom or a C_1 to C_{20} hydrocarbon group.)

[Chemical Formula 5]



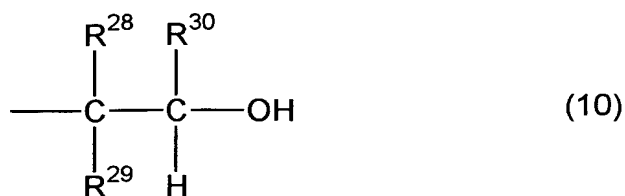
(In Formula 8, R^{19} to R^{21} may be the same or different, and each is a hydrogen atom or a C_1 to C_8 hydrocarbon group, R^{22} is a C_2 to C_{20} divalent ether bonded oxygen-containing hydrocarbon group or a C_1 to C_{10} divalent hydrocarbon group, R^{23} is a C_1 to C_{20} hydrocarbon group, t is a number whose average value is from 0 to 10, and when the terminal structures expressed by General Formula 8 have a plurality of R^{22}O groups, the plurality of R^{22}O groups may be the same or different.)

[Chemical Formula 6]



(In Formula (9), R^{24} to R^{27} may be the same or different, and each is a hydrogen atom or a C_1 to C_{20} hydrocarbon group.)

[Chemical Formula 7]



(In Formula (10), R^{28} to R^{30} may be the same or different, and each is a hydrogen atom or a C_1 to C_8 hydrocarbon group.)

[0118] Of these polyvinyl ethers, the following are particularly favorable examples.

(I) One having a structure in which one of the terminals is expressed by General Formula (6) or (7) and the other is expressed by General Formula (8) or (9), R^1 to R^3 in General Formula (4) are all hydrogen atoms, s is a number from 0 to 4, R^4 is a C_2 to C_4 divalent hydrocarbon group, and R^5 is a C_1 to C_{20} hydrocarbon group.

(II) One having only structural units expressed by General Formula (4), having a structure in which one of the terminals is expressed by General Formula (6) and the other is expressed by General Formula (7), R^1 to R^3 in General Formula (4) are all hydrogen atoms, s is a number from 0 to 4, R^4 is a C_2 to C_4 divalent hydrocarbon group, and R^5 is a C_1 to C_{20} hydrocarbon group.

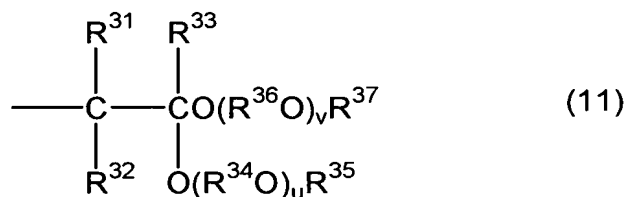
(III) One having a structure in which one of the terminals is expressed by General Formula (6) or (7) and the other is expressed by General Formula (8), R^1 to R^3 in General Formula (4) are all hydrogen atoms, s is a number from 0 to 4, R^4 is a C_2 to C_4 divalent hydrocarbon group, and R^5 is a C_1 to C_{20} hydrocarbon group.

(IV) One having only structural units expressed by General Formula (4), having a structure in which one of the terminals is

expressed by General Formula (6) and the other is expressed by General Formula (9), R^1 to R^3 in General Formula (4) are all hydrogen atoms, s is a number from 0 to 4, R^4 is a C_2 to C_4 divalent hydrocarbon group, and R^5 is a C_1 to C_{20} hydrocarbon group.

5 [0119] A polyvinyl ether compound having structural units expressed by General Formula (4) and having a structure in which one of the terminals is expressed by General Formula (6) and the other is expressed by the following General Formula (11) can also be used in the present invention.

10 [Chemical Formula 8]



(In Formula (11), R^{31} to R^{33} may be the same or different, and each is a hydrogen atom or a C_1 to C_8 hydrocarbon group, R^{34} and R^{36} may be the same or different, and each is a C_2 to C_{10} divalent hydrocarbon group, R^{35} and R^{37} may be the same or different, and each is a C_1 to C_{10} divalent hydrocarbon group, u and v may be the same or different, and each is a number whose average value is from 0 to 10, and when the terminal structures expressed by General Formula (11) have a plurality of $R^{34}\text{O}$ or $R^{36}\text{O}$ groups, the plurality of $R^{34}\text{O}$ or $R^{36}\text{O}$ groups may be the same or different.)

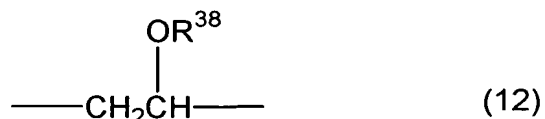
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[0120] Further, a polyvinyl ether compound composed of a homopolymer or copolymer of an alkyl vinyl ether composed of structural units expressed by the following General Formula (12) or (13),

in which the weight average molecular weight is from 300 to 5000, and having a structure in which one of the terminals is expressed by the following General Formula (14) or (15), can also be used in the present invention.

5 [Chemical Formula 9]



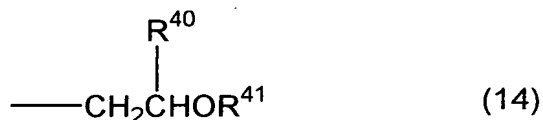
(In Formula (12), R^{38} is a C_1 to C_8 hydrocarbon group.)

[Chemical Formula 10]



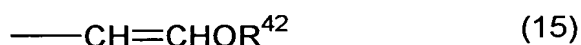
10 (In Formula (13), R^{39} is a C_1 to C_8 hydrocarbon group.)

[Chemical Formula 11]



(In Formula (14), R^{40} is a C_1 to C_3 alkyl group, and R^{41} is a C_1 to C_8 hydrocarbon group.)

15 [Chemical Formula 12]



(In Formula (15), R^{42} is a C_1 to C_8 hydrocarbon group.)

[0121] One or more other base oils can also be used in combination with the esters (A-1) and (A-2) in the present invention, but
20 an alkylbenzene, an ester oil other than the esters (A-1) and (A-2), or a polyvinyl ether can be used preferably as the base for a package air conditioner refrigerating oil.

[0122] There are no particular restrictions on the amount in which

these other base oils are contained in the present invention, but in terms of striking a good balance between performance characteristics such as oil return characteristics, lubricity, and stability, the amount is preferably not greater than 50 % by mass, and more preferably not greater than 30 % by mass, and even more preferably not greater than 10 % by mass, with respect to the total amount of the composition, and it is best if no other base oil is contained at all.

[0123] From the standpoint the effect on lubricity, stability, miscibility, and other performance aspects, the amount in which base oils other than the polyol ester (A) are contained is preferably not greater than 30 % by mass, and more preferably not greater than 20 % by mass, and even more preferably not greater than 10 % by mass, with 5 % by mass or less being particularly favorable. It is best if the refrigerating machine oil composition of the present invention contains no base oil other than the polyol ester (A).

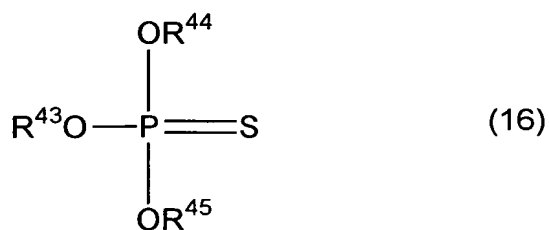
[0124] If the refrigerating machine oil composition of the present invention contains a mixed base oil of the ester (A-1) and the ester (A-2), then in terms of striking a good balance between performance characteristics such as oil return characteristics, lubricity, and stability, the amount in which base oils other than this mixed base oil are contained is preferably not greater than 50 % by mass, and more preferably not greater than 30 % by mass, and even more preferably not greater than 10 % by mass, and it is best if no base oil other than the mixed base oil of the ester (A-1) and the ester (A-2) is contained at all.

[0125] Phosphorothionate

The refrigerating machine oil composition of the present invention

contains a phosphorothionate (B). The compounds expressed by the following General Formula (16) can be used favorably as this phosphorothionate (B).

[Chemical Formula 13]



[0126] In Formula (16), R^{43} , R^{44} , and R^{45} may be the same or different, and each is a C_1 to C_{24} hydrocarbon group. Specific examples of the C_1 to C_{24} hydrocarbon group expressed by R^{43} to R^{45} include an alkyl group, cycloalkyl group, alkenyl group, alkylcycloalkyl group, aryl group, alkylaryl group, and arylalkyl group.

[0127] Examples of alkyl groups include a methyl group, ethyl group, propyl group, butyl group, pentyl group, hexyl group, heptyl group, octyl group, nonyl group, decyl group, undecyl group, dodecyl group, tridecyl group, tetradecyl group, pentadecyl group, hexadecyl group, heptadecyl group, octadecyl group, and other such alkyl groups (these alkyl groups may be linear or branched).

[0128] Examples of cycloalkyl groups include a cyclopentyl group, cyclohexyl group, cycloheptyl group, and other such C_5 to C_7 cycloalkyl groups. Examples of the above-mentioned alkylcycloalkyl groups include a methylcyclopentyl group, dimethylcyclopentyl group, methylethylcyclopentyl group, diethylcyclopentyl group, methylcyclohexyl group, dimethylcyclohexyl group, methylethylcyclohexyl group, diethylcyclohexyl group,

methylcycloheptyl group, dimethylcycloheptyl group, methylethylcycloheptyl group, diethylcycloheptyl group, and other such C₆ to C₁₁ alkylcycloalkyl groups (the alkyl group may be substituted at any position on the cycloalkyl group).

5 [0129] Examples of alkenyl groups include a butenyl group, pentenyl group, hexenyl group, heptenyl group, octenyl group, nonenyl group, decenyl group, undecenyl group, dodecenyl group, tridecenyl group, tetradecenyl group, pentadecenyl group, hexadecenyl group, heptadecenyl group, octadecenyl group, and other such alkenyl groups
10 (these alkenyl groups may be linear or branched, and the double bonds may be at any position).

[0130] Examples of aryl groups include a phenyl group, naphthyl group, and other such aryl groups. Examples of the above-mentioned alkylaryl groups include a tolyl group, xylyl group, ethylphenyl group,
15 propylphenyl group, butylphenyl group, pentylphenyl group, hexylphenyl group, heptylphenyl group, octylphenyl group, nonylphenyl group, decylphenyl group, undecylphenyl group, dodecylphenyl group, and other such C₇ to C₁₈ alkylaryl groups (the alkyl groups may be either linear or branched, and may be substituted at any position on the aryl
20 group).

[0131] Examples of arylalkyl groups include a benzyl group, phenylethyl group, phenylpropyl group, phenylbutyl group, phenylpentyl group, phenylhexyl group, and other such C₇ to C₁₂ arylalkyl groups the alkyl groups may be either linear or branched).

25 [0132] The C₁ to C₂₄ hydrocarbon group expressed by R⁴³ to R⁴⁵ above is preferably an alkyl group, aryl group, or alkylaryl group, and

more preferably a C₄ to C₁₈ alkyl group, C₇ to C₂₄ alkylaryl group, or phenyl group.

[0133] Specific examples of the phosphorothionate expressed by General Formula (16) include tributyl phosphorothionate, tripentyl phosphorothionate, trihexyl phosphorothionate, triheptyl phosphorothionate, trioctyl phosphorothionate, trinonyl phosphorothionate, tridecyl phosphorothionate, triundecyl phosphorothionate, tridodecyl phosphorothionate, tritridecyl phosphorothionate, tritetradecyl phosphorothionate, tripentadecyl phosphorothionate, trihexadecyl phosphorothionate, triheptadecyl phosphorothionate, trioctadecyl phosphorothionate, trioleyl phosphorothionate, triphenyl phosphorothionate, tricresyl phosphorothionate, trixylenyl phosphorothionate, cresyl diphenyl phosphorothionate, xylenyl diphenyl phosphorothionate, tris(n-propyl phenyl) phosphorothionate, tris(isopropyl phenyl) phosphorothionate, tris(n-butyl phenyl) phosphorothionate, tris(isobutyl phenyl) phosphorothionate, tris(s-butyl phenyl) phosphorothionate, and tris(t-butyl phenyl) phosphorothionate. Mixtures of these can also be used.

[0134] The amount in which the phosphorothionate (B) is contained in the refrigerating machine oil composition of the present invention is preferably from 0.01 to 5 % by mass with respect to the total amount of the composition. If the phosphorothionate content is set within the above range, the anti-wear property and stability (and particularly the thermal and oxidation stability) of the refrigerating oil composition can be further enhanced. More specifically, from the

standpoint of obtaining a high level of anti-wear property, the amount in which the phosphorothionate is added is preferably not less than 0.01 % by mass, and more preferably not less than 0.1 % by mass. Increasing the content over this amount will not have a corresponding effect of reducing wear, and on the contrary may actually lower stability or result in corrosive wear, so the phosphorothionate content is preferably not greater than 5 % by mass, and more preferably not greater than 3 % by mass, and even more preferably not greater than 1 % by mass.

[0135] Phosphorus-Based Additive

The refrigerating machine oil composition of the present invention further contains a phosphorus-based additive (C) (a phosphorus-based additive other than the abovementioned phosphorothionate). The phosphorus-based additive (C) is preferably at least one type of phosphorus compound selected from the group consisting of phosphoric acid esters, acidic phosphoric acid esters, amine salts of acidic phosphoric acid esters, chlorinated phosphoric acid esters, and phosphorous acid esters. These phosphorus compounds are esters of phosphoric acid or phosphorous acid and an alkanol, or polyether type of alcohol, or derivatives of these esters.

[0136] Examples of phosphoric acid esters include tributyl phosphate, tripentyl phosphate, trihexyl phosphate, triheptyl phosphate, trioctyl phosphate, trinonyl phosphate, tridecyl phosphate, triundecyl phosphate, tridodecyl phosphate, tritridecyl phosphate, tritetradecyl phosphate, tripentadecyl phosphate, trihexadecyl phosphate, triheptadecyl phosphate, trioctadecyl phosphate, trioleyl phosphate, triphenyl phosphate, tricresyl phosphate, trixylyl phosphate, cresyl

diphenyl phosphate, and xylenyl diphenyl phosphate.

[0137] Examples of acidic phosphoric esters include monobutyl acid phosphate, monopentyl acid phosphate, monohexyl acid phosphate, monoheptyl acid phosphate, monooctyl acid phosphate, monononyl acid phosphate, monodecyl acid phosphate, monoundecyl acid phosphate, monododecyl acid phosphate, monotridecyl acid phosphate, monotetradecyl acid phosphate, monopentadecyl acid phosphate, monohexadecyl acid phosphate, monoheptadecyl acid phosphate, monooctadecyl acid phosphate, monooleyl acid phosphate, dibutyl acid phosphate, dipentyl acid phosphate, dihexyl acid phosphate, diheptyl acid phosphate, dioctyl acid phosphate, dinonyl acid phosphate, didecyl acid phosphate, diundecyl acid phosphate, didodecyl acid phosphate, ditridecyl acid phosphate, ditetradecyl acid phosphate, dipentadecyl acid phosphate, dihexadecyl acid phosphate, diheptadecyl acid phosphate, dioctadecyl acid phosphate, and dioleyl acid phosphate.

[0138] Examples of amine salts of acidic phosphoric esters include salts of the above-mentioned acidic phosphoric esters and amines such as methylamine, ethylamine, propylamine, butylamine, pentylamine, hexylamine, heptylamine, octylamine, dimethylamine, diethylamine, dipropylamine, dibutylamine, dipentylamine, dihexylamine, diheptylamine, dioctylamine, trimethylamine, triethylamine, tripropylamine, tributylamine, tripentylamine, trihexylamine, triheptylamine and trioctylamine.

[0139] Examples of chlorinated phosphoric esters include tris-dichloropropyl phosphate, tris-chloroethyl phosphate, tris-chlorophenyl phosphate, and polyoxyalkylene bis[di(chloroalkyl)] phosphate.

[0140] Examples of phosphorous esters include dibutyl phosphite, dipentyl phosphite, dihexyl phosphite, diheptyl phosphite, dioctyl phosphite, dinonyl phosphite, didecyl phosphite, diundecyl phosphite, didodecyl phosphite, dioleyl phosphite, diphenyl phosphite, dicresyl phosphite, tributyl phosphite, tripentyl phosphite, trihexyl phosphite, triheptyl phosphite, trioctyl phosphite, trinonyl phosphite, tridecyl phosphite, triundecyl phosphite, tridodecyl phosphite, trioleyl phosphite, triphenyl phosphite, and tricresyl phosphite. The mixtures of these can also be used.

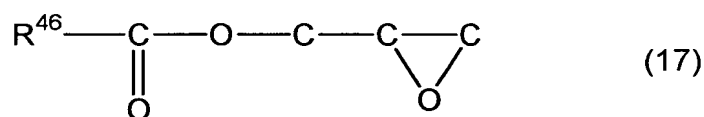
[0141] The amount in which the phosphorus-based additive (C) is contained in the refrigerating machine oil composition of the present invention is preferably from 0.01 to 5.0 % by mass with respect to the total amount of the composition. The anti-wear property and stability (and particularly the thermal and oxidation stability) can be further enhanced by setting the amount in which the ester-based additive is contained to within the above range. More specifically, from the standpoint of obtaining a high level of anti-wear property, the amount in which the phosphorus-based additive is added is preferably not less than 0.01 % by mass, and more preferably not less than 0.1 % by mass. Increasing the content over this amount will not have a corresponding effect of reducing wear, and on the contrary may actually lower stability or result in corrosive wear, so the phosphorus-based additive content is preferably not greater than 5 % by mass, and more preferably not greater than 4 % by mass, and even more preferably not greater than 3 % by mass.

[0142] Glycidyl Ester Epoxy Compound

The refrigerating machine oil composition of the present invention further contains a glycidyl ester epoxy compound (D) in addition to the phosphorothionate (B) and the phosphorus-based additive (C). The effect of achieving both good stability and good anti-wear property in the present invention is the result of the synergistic action of these three components. Also, the glycidyl ester epoxy compound (D) used in the present invention is better than other epoxy compounds, such as glycidyl ether epoxy compounds or cyclohexene dioxide, in terms of its effect of increasing lubricity and suppressing corrosion of a metal catalyst when used as an epoxy-based additive to a refrigerating oil.

[0143] The compounds expressed by the following General Formula (17) are favorable examples of the glycidyl ester epoxy compound (D).

[Chemical Formula 14]



[0144] In Formula (17), R^{46} is a C_1 to C_{18} hydrocarbon group. Examples of such hydrocarbon groups include C_1 to C_{18} alkyl groups, C_2 to C_{18} alkenyl groups, C_5 to C_7 cycloalkyl groups, C_6 to C_{18} alkylcycloalkyl groups, C_6 to C_{10} aryl groups, C_7 to C_{18} alkylaryl groups, and C_7 to C_{18} arylalkyl groups. Of these, C_5 to C_{15} alkyl groups, C_2 to C_{15} alkenyl groups, and alkylphenyl groups having a phenyl group and a C_1 to C_4 alkyl group are preferable.

[0145] Specific examples of favorable glycidyl ester epoxy compounds include glycidyl-2,2-dimethyloctanoate, glycidyl benzoate, glycidyl-tert-butyl benzoate, glycidyl acrylate, and glycidyl methacrylate.

[0146] The amount in which the glycidyl ester epoxy compound (D) is contained in the refrigerating machine oil composition of the present invention is preferably from 0.01 to 5 % by mass with respect to the total amount of the composition. Setting the glycidyl ester epoxy compound (D) content to within the above range further enhances lubricity and stability (and particularly the thermal and oxidation stability). More specifically, from the standpoint of obtaining a high level of lubricity and stability, the amount in which the glycidyl ester epoxy compound (D) is added is preferably not less than 0.01 % by mass, and more preferably not less than 0.1 % by mass. Increasing the content over this amount will not have a corresponding effect, so the glycidyl ester epoxy compound (D) content is preferably not greater than 3 % by mass, and more preferably not greater than 2 % by mass.

[0147] As mentioned above, the refrigerating machine oil composition of the present invention contains the polyol ester (A) as a base oil, and contains the phosphorothionate (B), phosphorus-based additive (C), and glycidyl ester epoxy compound (D) as essential components, but may further contain an oiliness agent (E), benzotriazole and/or a derivative thereof (F), an epoxy compound other than a glycidyl ester epoxy compound (G), or other additives.

[0148] Oiliness Agent

Examples of oil-based agents include ester oiliness agents (E), monohydric alcohol oiliness agents, carboxylic acid oiliness agents, and ether oiliness agents.

[0149] An ester oiliness agent is obtained by reacting an alcohol with a carboxylic acid. The alcohol here may be either a monohydric

alcohol or a polyhydric alcohol. The carboxylic acid may be a monobasic acid or a polybasic acid.

[0150] The monohydric alcohol that constitutes the ester oiliness agent is usually one with a carbon number of 1 to 24, and preferably 1 to 12, and more preferably 1 to 8, and this alcohol may be linear or branched, and may be saturated or unsaturated. Specific examples of C₁ to C₂₄ alcohols include methanol, ethanol, linear or branched propanol, linear or branched butanol, linear or branched pentanol, linear or branched hexanol, linear or branched heptanol, linear or branched octanol, linear or branched nonanol, linear or branched decanol, linear or branched undecanol, linear or branched dodecanol, linear or branched tridecanol, linear or branched tetradecanol, linear or branched pentadecanol, linear or branched hexadecanol, linear or branched heptadecanol, linear or branched octadecanol, linear or branched nonadecanol, linear or branched eicosanol, linear or branched heneicosanol, linear or branched tricosanol, linear or branched tetracosanol, and mixtures of these.

[0151] The polyhydric alcohol that constitutes the ester oiliness agent is usually from dihydric to decahydric, and preferably dihydric to hexahydric. Specific examples of dihydric to decahydric alcohols include ethylene glycol, diethylene glycol, polyethylene glycol (trimer to pentadecamer of ethylene glycol), propylene glycol, dipropylene glycol, polypropylene glycol (trimer to pentadecamer of propylene glycol), 1,3-propanediol, 1,2-propanediol, 1,3-butanediol, 1,4-butanediol, 2-methyl-1,2-propanediol, 2-methyl-1,3-propanediol, 1,2-pentanediol, 1,3-pentanediol, 1,4-pentanediol, 1,5-pentanediol, neopentyl glycol, and

other such dihydric alcohols; glycerol, polyglycerol (dimer to octamer of glycerol, such as diglycerol, triglycerol, and tetraglycerol), trimethylolalkanes (such as trimethylolethane, trimethylolpropane, and trimethylolbutane) and dimer to octamer thereof, pentaerythritol and
 5 dimer to tetramer thereof, 1,2,4-butanetriol, 1,3,5-pentanetriol, 1,2,6-hexanetriol, 1,2,3,4-butanetetrol, sorbitol, sorbitan, sorbitol-glycerol condensate, adonitol, arabitol, xylytol, mannitol, and other polyhydric alcohols; xylose, arabinose, ribose, rhamnose, glucose, fructose, galactose, mannose, sorbose, cellobiose, maltose, isomaltose, trehalose,
 10 sucrose, and other such saccharides; and mixtures of these.

[0152] Of these polyhydric alcohols, preferable are ethylene glycol, diethylene glycol, polyethylene glycol (trimer to decamer of ethylene glycol), propylene glycol, dipropylene glycol, polypropylene glycol (trimer to decamer of propylene glycol), 1,3-propanediol, 2-methyl-
 15 1,2-propanediol, 2-methyl-1,3-propanediol, neopentyl glycol, glycerol, diglycerol, triglycerol, trimethylolalkanes (such as trimethylolethane, trimethylolpropane, and trimethylolbutane) and dimer to tetramer thereof, pentaerythritol, dipentaerythritol, 1,2,4-butanetriol, 1,3,5-pentanetriol, 1,2,6-hexanetriol, 1,2,3,4-butanetetrol, sorbitol, sorbitan, sorbitol-glycerol condensate, adonitol, arabitol, xylytol, mannitol, and other
 20 dihydric to hexahydric alcohols, and mixtures of these. Even more preferable are ethylene glycol, propylene glycol, neopentyl glycol, glycerol, trimethylolethane, trimethylolpropane, pentaerythritol, sorbitan, and mixtures of these. Of these, neopentyl glycol, trimethylolethane, trimethylolpropane, pentaerythritol, and mixtures of these are preferred.
 25

[0153] As mentioned above, the alcohol that constitutes the ester

oiliness agent may be a monohydric alcohol or a polyhydric alcohol, but in terms of further increasing anti-wear property and friction property, and in terms of preventing precipitation at low temperatures or under a refrigerant atmosphere, a monohydric alcohol is preferable.

5 [0154] Of the acids that can constitute the ester oiliness agent, a monobasic acid is usually a C₂ to C₂₄ fatty acid, which may be either linear or branched, and which may be either saturated or unsaturated. Specific examples include acetic acid, propionic acid, linear or branched butanoic acid, linear or branched pentanoic acid, linear or branched
10 hexanoic acid, linear or branched heptanoic acid, linear or branched octanoic acid, linear or branched nonanoic acid, linear or branched decanoic acid, linear or branched undecanoic acid, linear or branched dodecanoic acid, linear or branched tridecanoic acid, linear or branched tetradecanoic acid, linear or branched pentadecanoic acid, linear or
15 branched hexadecanoic acid, linear or branched heptadecanoic acid, linear or branched octadecanoic acid, linear or branched hydroxyoctadecanoic acid, linear or branched nonadecanoic acid, linear or branched eicosanoic acid, linear or branched heneicosanoic acid, linear or branched docosanoic acid, linear or branched tricosanoic acid,
20 linear or branched tetracosanoic acid, and other such saturated fatty acids; acrylic acid, linear or branched butenoic acid, linear or branched pentenoic acid, linear or branched hexenoic acid, linear or branched heptenoic acid, linear or branched octenoic acid, linear or branched nonenoic acid, linear or branched decenoic acid, linear or branched
25 undecenoic acid, linear or branched dodecenoic acid, linear or branched tridecenoic acid, linear or branched tetradecenoic acid, linear or

branched pentadecenoic acid, linear or branched hexadecenoic acid, linear or branched heptadecenoic acid, linear or branched octadecenoic acid, linear or branched hydroxyoctadecenoic acid, linear or branched nonadecenoic acid, linear or branched eicosenoic acid, linear or branched heneicosenoic acid, linear or branched docosenoic acid, linear or branched tricosenoic acid, linear or branched tetracosenoic acid, and other such unsaturated fatty acids; and mixtures of these.

[0155] Examples of polybasic acids include a dibasic acid and trimellitic acid, but in terms of preventing precipitation at low temperatures or under a refrigerant atmosphere, a dibasic acid is preferable. This dibasic acid may be either a chain-form dibasic acid or a cyclic dibasic acid. In the case of a chain-form dibasic acid, it may be either linear or branched, and may be either saturated or unsaturated. The chain-form dibasic acid is preferably a C₂ to C₁₆ chain-form dibasic acid, specific examples of which include ethane diacid, propane diacid, linear or branched butane diacid, linear or branched pentane diacid, linear or branched hexane diacid, linear or branched heptane diacid, linear or branched octane diacid, linear or branched nonane diacid, linear or branched decane diacid, linear or branched undecane diacid, linear or branched dodecane diacid, linear or branched tridecane diacid, linear or branched tetradecane diacid, linear or branched heptadecane diacid, linear or branched hexadecane diacid, linear or branched hexene diacid, linear or branched heptene diacid, linear or branched octene diacid, linear or branched nonene diacid, linear or branched decene diacid, linear or branched undecene diacid, linear or branched dodecene diacid, linear or branched tridecene diacid, linear or branched tetradecene diacid,

linear or branched heptadecene diacid, linear or branched hexadecene diacid, and mixtures of these. Examples of cyclic dibasic acids include 1,2-cyclohexanedicarboxylic acid, 4-cyclohexene-1,2-dicarboxylic acid, and aromatic dicarboxylic acid. Of these, chain-form dibasic acids are preferred.

[0156] As mentioned above, the acid that constitutes the ester oiliness agent may be either a monobasic acid or a polybasic acid, but in terms of enhancing anti-wear property and friction property, a monobasic acid is preferable.

[0157] There are no particular restrictions on how the alcohol and acid are combined in the ester oiliness agent, but examples include the following ester combinations (i) to (vii).

(i) an ester of a monohydric alcohol and a monobasic acid

(ii) an ester of a polyhydric alcohol and a monobasic acid

(iii) an ester of a monohydric alcohol and a polybasic acid

(iv) an ester of a polyhydric alcohol and a polybasic acid

(v) a mixed ester of a mixture of monohydric alcohol and polyhydric alcohol and a polybasic acid

(vi) a mixed ester of a polyhydric alcohol and a mixture of polybasic acid and monobasic acid

(vii) a mixed ester of a mixture of monohydric alcohol and polyhydric alcohol and a mixture of polybasic acid and monobasic acid

[0158] Each of the ester oiliness agents in (ii) to (vii) above may be a complete ester in which all of the hydroxyl groups of the polyhydric alcohol or the carboxyl groups of the polybasic acid have been esterified, or may be a partial ester in which some of the hydroxyl groups or

carboxyl groups remain, but a complete ester is preferable in terms of have less effect on the ability to prevent precipitation at low temperatures or under a refrigerant atmosphere, and a partial ester is preferable in terms of enhancing friction property.

5 [0159] Of the ester oiliness agents of (i) to (vii) above, an ester of a monohydric alcohol and a monobasic acid (i) or an ester of a monohydric alcohol and a polybasic acid (iii) is preferable, and the ester of (i) is best of all. These esters are extremely effective at enhancing anti-wear property and friction property, and have little effect on the
10 ability to prevent precipitation at low temperatures or under a refrigerant atmosphere.

[0160] In terms of further enhancing the anti-wear property and friction property, and in terms of thermal and oxidation stability, the carbon number of the monobasic acid in the ester oiliness agent of (i)
15 above is preferably not less than 10, and more preferably not less than 12, and even more preferably not less than 14. In terms of preventing precipitation at low temperatures or under a refrigerant atmosphere, the carbon number of the monobasic acid is preferably not greater than 28, and more preferably not greater than 26, and even more preferably not
20 greater than 24. Examples of such esters include methyl stearate, butyl stearate, methyl palmitate, and isopropyl palmitate.

[0161] The dibasic acid in the ester of (iii) above is preferably in chain form. Examples of such esters include diisodecyl adipate, diisononyl adipate, and diisobutyl adipate.

25 [0162] Of the above ester oiliness agents, it is preferable to use one or more types selected from among esters of a monohydric alcohol and a

monobasic acid, and esters of a chain-form dibasic acid and a monohydric alcohol.

[0163] Examples of monohydric alcohol oiliness agents include the monohydric alcohols listed as examples in the description of the ester oiliness agent above. From the standpoint of enhancing friction property and anti-wear property, the total carbon number of the monohydric alcohol oiliness agent is preferably not less than 6, and more preferably not less than 8, and even more preferably not less than 10. If the total carbon number is too large, there is the danger that precipitation will tend to occur in a refrigerant atmosphere, so the total carbon number is preferably not greater than 20, and more preferably not greater than 18, with not greater than 16 being best.

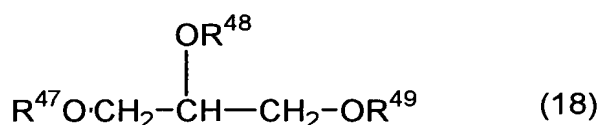
[0164] The carboxylic acid oiliness agent may be either a monobasic acid or a polybasic acid. Examples of this carboxylic acid include the monobasic acids and polybasic acids listed in the description of the ester oiliness agent. Of these, a monobasic acid is preferable in terms of friction property and anti-wear property. From the standpoint of enhancing friction property and anti-wear property, the total carbon number of the carboxylic acid oiliness agent is preferably not less than 6, and more preferably not less than 8, and even more preferably not less than 10. If the total carbon number of the carboxylic acid oiliness agent is too large, there is the danger that precipitation will tend to occur in a refrigerant atmosphere, so the total carbon number is preferably not greater than 20, and more preferably not greater than 18, with not greater than 16 being best.

[0165] Examples of ether oiliness agents include etherified

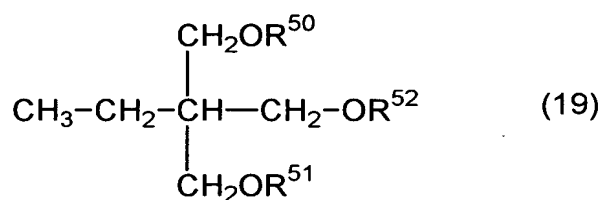
trivalent to hexavalent aliphatic polyhydric alcohols, and etherified bimolecular condensates and trimolecular condensates of trivalent to hexavalent aliphatic polyhydric alcohols.

5 [0166] Etherified trivalent to hexavalent aliphatic polyhydric alcohols are expressed by the following General Formulas (18) to (23), for example.

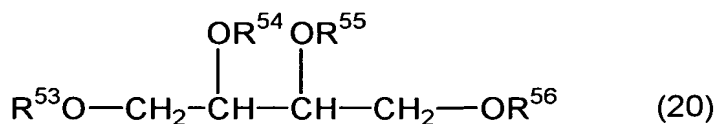
[Chemical Formula 15]



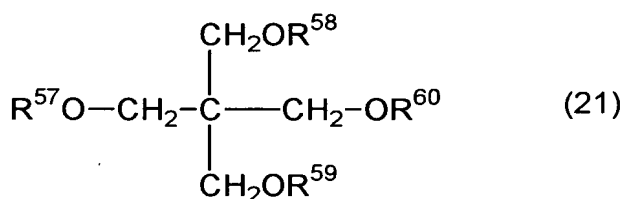
[Chemical Formula 16]



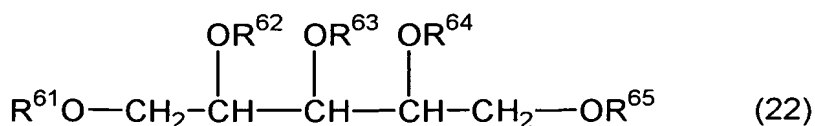
[Chemical Formula 17]



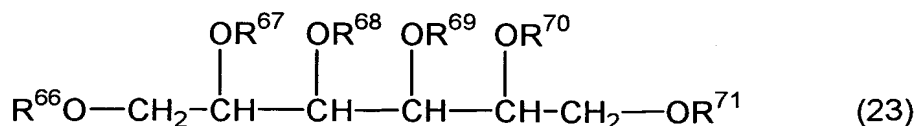
[Chemical Formula 18]



15 [Chemical Formula 19]



[Chemical Formula 20]



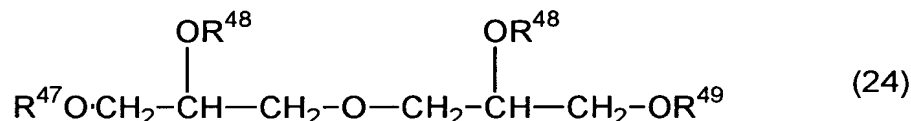
(In the formulas, R^{47} to R^{71} may be the same or different, and are each a hydrogen atom or a C_1 to C_{18} linear or branched alkyl group, aryl group, aralkyl group, or a glycol ether residue expressed by $-(\text{R}^a\text{O})_n-\text{R}^b$ (where R^a is a C_2 to C_6 alkylene group, R^b is a C_1 to C_{20} alkyl group, aryl group, or aralkyl group, and n is an integer from 1 to 10).)

[0167] Specific examples of trivalent to hexavalent aliphatic polyhydric alcohols include glycerol, trimethylolpropane, erythritol, pentaerythritol, arabitol, sorbitol, and mannitol. Examples of R^{47} to R^{71} in the above General Formulas (18) to (23) include a methyl group, ethyl group, n-propyl group, isopropyl group, various butyl groups, various pentyl groups, various hexyl groups, various heptyl groups, various octyl groups, various nonyl groups, various decyl groups, various undecyl groups, various dodecyl groups, various tridecyl groups, various tetradecyl groups, various pentadecyl groups, various hexadecyl groups, various heptadecyl groups, various octadecyl groups, a phenyl group, and a benzyl group. The above-mentioned etherified compound encompasses partially etherified compounds in which some of the R^{47} to R^{71} groups are hydrogen atoms.

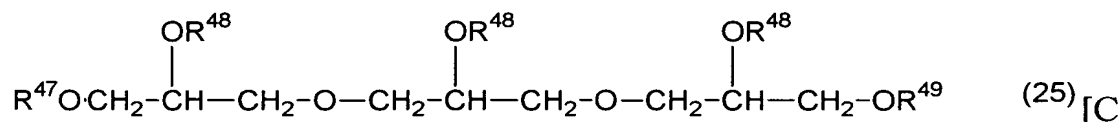
[0168] Examples of etherified bimolecular condensates and trimolecular condensates of trivalent to hexavalent aliphatic polyhydric alcohols include the same or different types of condensates of the compounds expressed by General Formulas (18) to (23). For instance, etherified bimolecular condensates and trimolecular condensates of the alcohols expressed by General Formula (18) are expressed by General

Formulas (24) and (25), respectively. Etherified bimolecular condensates and trimolecular condensates of the alcohols expressed by General Formula (21) are expressed by General Formulas (26) and (27), respectively.

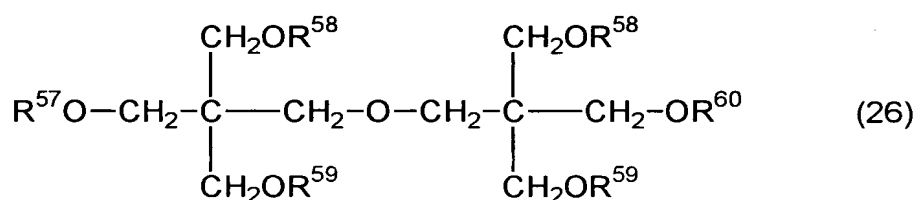
5 [Chemical Formula 21]



[Chemical Formula 22]

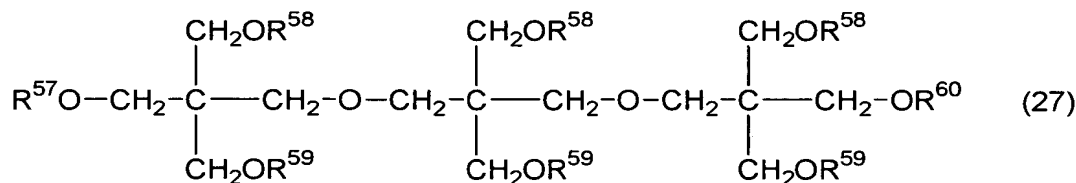


hemical Formula 23]



10

[Chemical Formula 24]



(In the formulas, R^{47} to R^{49} and R^{57} to R^{60} are defined the same as R^{47} to R^{49} in Formula (18) and R^{57} to R^{60} in Formula (21), respectively.)

15 [0169] Specific examples of bimolecular condensates and trimolecular condensates of trivalent to hexavalent aliphatic polyhydric alcohols include diglycerol, ditrimethylolpropane, dipentaerythritol, disorbitol, triglycerol, tritrimethylolpropane, tripentaerythritol, and trisorbitol.

[0170] Specific examples of the ether oiliness agents expressed by General Formulas (18) to (23) include a trihexyl ether of glycerol, dimethyloctyl triether of glycerol, di(methyloxyisopropylene)dodecyl triether of glycerol, diphenyloctyl triether of glycerol, di(phenyloxyisopropylene)dodecyl triether of glycerol, trihexyl ether of trimethylolpropane, dimethyloctyl triether of trimethylolpropane, di(methyloxyisopropylene)dodecyl triether of trimethylolpropane, tetrahexyl ether of pentaerythritol, trimethyloctyl tetraether of pentaerythritol, tri(methyloxyisopropylene)dodecyl tetraether of pentaerythritol, hexapropyl ether of sorbitol, tetramethyloctyl pentaether of sorbitol, hexa(methyloxyisopropylene) ether of sorbitol, tetrabutyl ether of diglycerol, dimethyldioctyl tetraether of diglycerol, tri(methyloxyisopropylene)dodecyl tetraether of diglycerol, pentaethyl ether of triglycerol, trimethyldioctyl pentaether of triglycerol, tetra(methyloxyisopropylene)decyl pentaether of triglycerol, tetrabutyl ether of ditrimethylolpropane, dimethyldioctyl tetraether of ditrimethylolpropane, tri(methyloxyisopropylene)dodecyl tetraether of ditrimethylolpropane, pentaethyl ether of tritrimethylolpropane, trimethyldioctyl pentaether of tritrimethylolpropane, tetra(methyloxyisopropylene)decyl pentaether of tritrimethylolpropane, hexapropyl ether of dipentaerythritol, pentamethyloctyl hexaether of dipentaerythritol, hexa(methyloxyisopropylene) ether of dipentaerythritol, octapropyl ether of tripentaerythritol, pentamethyloctyl hexaether of tripentaerythritol, hexa(methyloxyisopropylene) of tripentaerythritol, octamethyldioctyl decaether of disorbitol, and deca(methyloxyisopropylene) ether of disorbitol. Of these, a

diphenyloctyl triether of glycerol, di(methyloxyisopropylene)dodecyl triether of trimethylolpropane, tetrahexyl ether of pentaerythritol, hexapropyl ether of sorbitol, dimethyldioctyl tetraether of diglycerol, tetra(methyloxyisopropylene)decyl pentaether of triglycerol, hexapropyl ether of dipentaerythritol, and pentamethyloctyl hexaether of tripentaerythritol are preferable.

[0171] Of the above-mentioned ester oiliness agents, monohydric alcohol oiliness agents, carboxylic acid oiliness agents, and ether oiliness agents, as long as it is used along with the phosphorothionate (B), the phosphorus-based additive (C), and the glycidyl ester epoxy compound (D) in the refrigerating machine oil composition of the present invention, just one type of oiliness agent may be used alone, or a combination of two or more types may be used. Of these oiliness agents, ester oiliness agents and ether oiliness agents are preferred in terms of being able to achieve good friction property and anti-wear property. Not only do they afford better anti-wear property and friction property, but ester oiliness agents and ether oiliness agents are also better at preventing precipitation than monohydric alcohol oiliness agents, and have better stability than carboxylic acid oiliness agents.

[0172] The oiliness agent (E) may be contained in any amount desired, but in terms of obtaining better anti-wear property and friction property, the amount is preferably not less than 0.01 % by mass, and more preferably not less than 0.05 % by mass, and even more preferably not less than 0.1 % by mass with respect to the total amount of the composition. In terms of preventing precipitation at low temperatures and under a refrigerant atmosphere, and of obtaining better thermal and

oxidation stability in the refrigerating oil composition, this content is preferably not greater than 10 % by mass, and more preferably not greater than 7.5 % by mass, and even more preferably not greater than 5 % by mass with respect to the total amount of the composition.

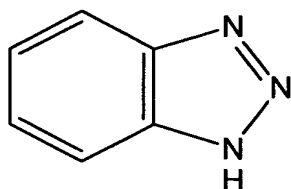
5 [0173] From the standpoint of further improving anti-wear property and friction property, the ratio (weight ratio) of the combined amount in which the phosphorothionate (B), the phosphorus-based additive (C), and the glycidyl ester epoxy compound (D) are contained to the amount in which the oiliness agent (E) is contained is preferably
10 from 1:10 to 10:1, and more preferably 1:5 to 5:1, and even more preferably 1:3 to 1:1.

[0174] Benzotriazole and/or Derivative Thereof

[0175] The refrigerating machine oil composition of the present invention preferably further contains benzotriazole and/or a derivative thereof (F). The effect of enhancing anti-wear property and friction
15 property can be further enhanced by having benzotriazole and/or a derivative thereof (F) contained.

[0176] Benzotriazole is a compound expressed by the following Formula (28).

20 [Chemical Formula 25]

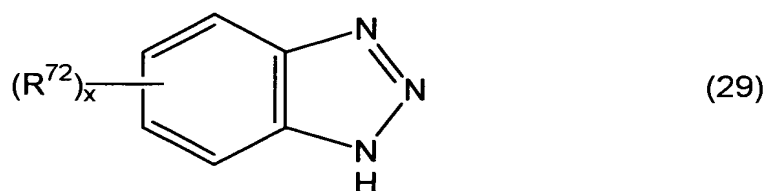


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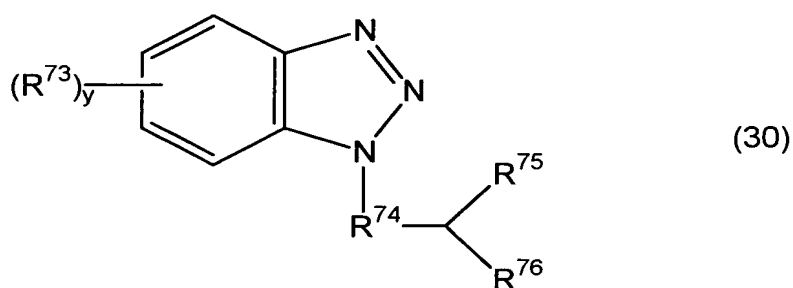
[0177] Examples of benzotriazole derivatives include the alkylbenzotriazoles expressed by the following General Formula (29),

and the (alkyl)aminoalkylbenzotriazoles expressed by the following General Formula (30).

[Chemical Formula 26]



5 [Chemical Formula 27]



[0178] In Formula (29) above, R^{72} is a C_1 to C_4 linear or branched alkyl group, and preferably a methyl group or ethyl group, and x is a number from 1 to 3, and preferably 1 or 2. Examples of R^{72} include a methyl group, ethyl group, n-propyl group, isopropyl group, n-butyl group, isobutyl group, sec-butyl group, and tert-butyl group. In terms of especially good prevention of oxidation, it is preferable that R^{72} is a methyl group or ethyl group and x is a number from 1 or 2. Examples of the alkylbenzotriazoles expressed by General Formula (14) include methylbenzotriazole (tolyltriazole), dimethylbenzotriazole, ethylbenzotriazole, ethylmethylbenzotriazole, diethylbenzotriazole, and mixtures of these.

[0179] In Formula (30) above, R^{73} is a C_1 to C_4 linear or branched alkyl group, and preferably a methyl group or ethyl group, R^{74} is a

methyl group or ethyl group, R^{75} and R^{76} may be the same or different
 and are each a hydrogen atom or a C_1 to C_{18} linear or branched alkyl
 group, and preferably a C_1 to C_{12} linear or branched alkyl group, and y is
 a number from 0 to 3, and preferably 0 or 1. Examples of R^{73} include a
 5 methyl group, ethyl group, n-propyl group, isopropyl group, n-butyl
 group, isobutyl group, sec-butyl group, tert-butyl group. Examples of
 R^{73} and R^{76} include independently a hydrogen atom, methyl group, ethyl
 group, propyl group, isopropyl group, n-butyl group, isobutyl group,
 sec-butyl group, tert-butyl group, linear or branched pentyl group, linear
 10 or branched hexyl group, linear or branched heptyl group, linear or
 branched octyl group, linear or branched nonyl group, linear or branched
 decyl group, linear or branched undecyl group, linear or branched
 dodecyl group, linear or branched tridecyl group, linear or branched
 tetradecyl group, linear or branched pentadecyl group, linear or branched
 15 hexadecyl group, linear or branched heptadecyl group, linear or branched
 octadecyl group, or other such alkyl group.

[0180] In terms of especially good prevention of oxidation, the
 (alkyl)aminobenzotriazole expressed by Formula (30) above is
 preferably a dialkylaminoalkylbenzotriazole or
 20 dialkylaminoalkyltolyltriazole in which R^{73} is a methyl group, y is 0 or 1,
 R^{74} is a methylene group or ethylene group, and R^{75} and R^{76} are each a
 C_1 to C_{12} linear or branched alkyl group, or a mixture of these
 compounds. Examples of these dialkylaminoalkylbenzotriazoles include
 dimethylaminomethylbenzotriazole, diethylaminomethylbenzotriazole,
 25 di-(linear or branched) propylaminomethylbenzotriazole, di-(linear or
 branched) butylaminomethylbenzotriazole, di-(linear or branched)

	pentylaminomethylbenzotriazole,	di-(linear	or	branched)
	hexylaminomethylbenzotriazole,	di-(linear	or	branched)
	heptylaminomethylbenzotriazole,	di-(linear	or	branched)
	octylaminomethylbenzotriazole,	di-(linear	or	branched)
5	nonylaminomethylbenzotriazole,	di-(linear	or	branched)
	decylaminomethylbenzotriazole,	di-(linear	or	branched)
	undecylaminomethylbenzotriazole,	di-(linear	or	branched)
	dodecylaminomethylbenzotriazole;	dimethylaminoethylbenzotriazole,		
	diethylaminoethylbenzotriazole,	di-(linear	or	branched)
10	propylaminoethylbenzotriazole,	di-(linear	or	branched)
	butylaminoethylbenzotriazole,	di-(linear	or	branched)
	pentylaminoethylbenzotriazole,	di-(linear	or	branched)
	hexylaminoethylbenzotriazole,	di-(linear	or	branched)
	heptylaminoethylbenzotriazole,	di-(linear	or	branched)
15	octylaminoethylbenzotriazole,	di-(linear	or	branched)
	nonylaminoethylbenzotriazole,	di-(linear	or	branched)
	decylaminoethylbenzotriazole,	di-(linear	or	branched)
	undecylaminoethylbenzotriazole,	di-(linear	or	branched)
	dodecylaminoethylbenzotriazole;	dimethylaminomethyltolyltriazole,		
20	diethylaminomethyltolyltriazole,	di-(linear	or	branched)
	propylaminomethyltolyltriazole,	di-(linear	or	branched)
	butylaminomethyltolyltriazole,	di-(linear	or	branched)
	pentylaminomethyltolyltriazole,	di-(linear	or	branched)
	hexylaminomethyltolyltriazole,	di-(linear	or	branched)
25	heptylaminoethyltolyltriazole,	di-(linear	or	branched)
	octylaminomethyltolyltriazole,	di-(linear	or	branched)

	nonylaminomethyltolyltriazole,	di-(linear	or	branched)
	decylaminomethyltolyltriazole,	di-(linear	or	branched)
	undecylaminomethyltolyltriazole,	di-(linear	or	branched)
	dodecylaminomethyltolyltriazole;	dimethylaminoethyltolyltriazole,		
5	diethylaminoethyltolyltriazole,	di-(linear	or	branched)
	propylaminoethyltolyltriazole,	di-(linear	or	branched)
	butylaminoethyltolyltriazole,	di-(linear	or	branched)
	pentylaminoethyltolyltriazole,	di-(linear	or	branched)
	hexylaminoethyltolyltriazole,	di-(linear	or	branched)
10	heptylaminoethyltolyltriazole,	di-(linear	or	branched)
	octylaminoethyltolyltriazole,	di-(linear	or	branched)
	nonylaminoethyltolyltriazole,	di-(linear	or	branched)
	decylaminoethyltolyltriazole,	di-(linear	or	branched)
	undecylaminoethyltolyltriazole,	di-(linear	or	branched)
15	dodecylaminoethyltolyltriazole; and mixtures of these.			

[0181] The benzotriazole and/or a derivative thereof (F) may be contained in any amount desired in the refrigerating machine oil composition of the present invention, but the amount is preferably not less than 0.001 % by mass, and more preferably not less than 0.005 % by mass, with respect to the total amount of the composition. If the amount is less than 0.001 % by mass, the benzotriazole and/or a derivative thereof may not have the intended effect of enhancing anti-wear property and friction property. Also, the benzotriazole and/or a derivative thereof (F) is preferably contained in an amount of not greater than 1.0 % by mass, and more preferably not greater than 0.5 % by mass, with respect to the total amount of the composition. If the amount exceeds 1.0 % by

mass, there may be no corresponding additional effect of enhancing anti-wear property and friction property, so exceeding this amount is undesirable from a cost standpoint.

[0182] Epoxy Compound other than Glycidyl Ester Epoxy Compound

The refrigerating machine oil composition of the present invention may further contain any of the epoxy compounds listed as G-1 to G-7 below, in addition to the glycidyl ester epoxy compound (D). The epoxy compounds G-1 to G-7 may be used singly or in combinations of two or more types.

G-1: phenylglycidyl ether epoxy compound

G-2: alkylglycidyl ether epoxy compound

G-3: allyloxirane compound

G-4: alkyloxirane compound

G-5: alicyclic epoxy compound

G-6: epoxidized fatty acid monoester

G-7: epoxidized vegetable oil

[0183] Specific examples of phenylglycidyl ether epoxy compounds G-1 include phenylglycidyl ether and alkylphenylglycidyl ether. Examples of the alkylphenylglycidyl ether referred to here include those having from one to three C₁ to C₁₃ alkyl groups, of which those having one C₄ to C₁₀ alkyl group is preferable, examples of which include n-butylphenylglycidyl ether, i-butylphenylglycidyl ether, sec-butylphenylglycidyl ether, tert-butylphenylglycidyl ether, pentylphenylglycidyl ether, hexylphenylglycidyl ether, heptylphenylglycidyl ether, octylphenylglycidyl ether,

nonylphenylglycidyl ether, and decylphenylglycidyl ether.

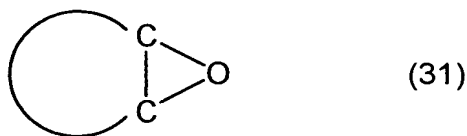
[0184] Specific examples of alkylglycidyl ether epoxy compounds G-2 include decylglycidyl ether, undecylglycidyl ether, dodecylglycidyl ether, tridecylglycidyl ether, tetradecylglycidyl ether, 2-ethylhexylglycidyl ether, neopentylglycoldiglycidyl ether, trimethylolpropane triglycidyl ether, pentaerythritol tetraglycidyl ether, 1,6-hexanediol diglycidyl ether, sorbitolpolyglycidyl ether, polyalkyleneglycol monoglycidyl ether, and polyalkyleneglycol diglycidyl ether.

[0185] Specific examples of allyloxirane compounds G-3 include 1,2-epoxystyrene and alkyl-1,2-epoxystyrene.

[0186] Specific examples of alkyloxirane compounds G-4 include 1,2-epoxybutane, 1,2-epoxypentane, 1,2-epoxyhexane, 1,2-epoxyheptane, 1,2-epoxyoctane, 1,2-epoxynonane, 1,2-epoxydecane, 1,2-epoxyundecane, 1,2-epoxydodecane, 1,2-epoxytridecane, 1,2-epoxytetradecane, 1,2-epoxypentadecane, 1,2-epoxyhexadecane, 1,2-epoxyheptadecane, 1,1,2-epoxyoctadecane, 2-epoxynonadecane and 1,2-epoxyeicosane.

[0187] Specific examples of alicyclic epoxy compounds G-5 include compounds in which carbon atoms constituting the epoxy groups directly constitute the alicyclic ring, such as compounds expressed by General Formula (31) below.

[Chemical Formula 28]



[0188] Specific examples of alicyclic epoxy compounds include

1,2-epoxycyclohexane, 1,2-epoxycyclopentane, 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate, bis(3,4-epoxycyclohexylmethyl) adipate, exo-2,3-epoxynorbornane, bis(3,4-epoxy-6-methylcyclohexylmethyl) adipate, 2-(7-oxabicyclo[4.1.0]hept-3-yl)-spiro(1,3-dioxane-5,3'-[7]oxabicyclo[4.1.0]heptane, 4-(1'-methylepoxyethyl)-1,2-epoxy-2-methylcyclohexane, and 4-epoxyethyl-1,2-epoxycyclohexane.

[0189] Specific examples of epoxidized fatty acid monoesters G-6 include esters of epoxidized C₁₂ to C₂₀ fatty acids and C₁ to C₈ alcohols, phenols, or alkylphenols. It is particularly favorable to use a butyl, hexyl, benzyl, cyclohexyl, methoxyethyl, octyl, phenyl, or butylphenyl ester of epoxystearic acid.

[0190] Specific examples of epoxidized vegetable oils G-7 include epoxy compounds of vegetable oils such as soybean oil, linseed oil, and cottonseed oil.

[0191] Among these epoxy compounds, phenylglycidyl ether epoxy compounds, alicyclic epoxy compounds, and epoxidized fatty acid monoesters are preferred because thermal and hydrolytic stability can be increased further, with alicyclic epoxy compounds being particularly favorable.

[0192] When these epoxy compounds are contained in the refrigerating machine oil composition of the invention, there are no particular restrictions on the amount in which they are contained, but the total amount of other epoxy compounds added is preferably 0.1 to 5.0 % by mass, and more preferably 0.2 to 2.0 % by mass, with respect to the total amount of the composition.

[0193] Other Additives

In order to further improve performance, known refrigerating oil additives can be added as needed to the refrigerating machine oil composition of the present invention, examples of which include phenol-based antioxidants such as di-tert-butyl-p-cresol and bisphenol A; amine-based antioxidants such as phenyl- α -naphthylamide and N,N-di(2-naphthyl)-p-phenylenediamine; anti-wear agents such as zinc dithiophosphate; extreme pressure agents such as chlorinated paraffin and sulfur compounds; oiliness agents such as fatty acids; antifoaming agents such as those based on silicone; viscosity index improvers; pour-point depressants; detergent dispersants; and other such additives, either alone or in combinations of two or more types. There are no particular restrictions on the total amount in which these additives are added, but this amount is preferably not greater than 10 % by mass, and more preferably not greater than 5 % by mass, with respect to the total amount of the composition.

[0194] Properties of Refrigerating Oil Composition

There are no particular restrictions on the volume resistivity of the refrigerating machine oil composition of the invention, but it is preferably not less than $1.0 \times 10^9 \Omega \cdot \text{cm}$. In particular, when the composition is used for a closed type of refrigerating machine, high electrical insulation tends to be necessary. The term "volume resistivity" as used in the present invention means the value ($\Omega \cdot \text{cm}$) at 25°C as measured according to JIS C 2101 "Electric Insulating Oil Testing Method."

[0195] There are no particular restrictions on the moisture content

of the refrigerating machine oil composition of the invention, but it is preferably not greater than 200 ppm, more preferably not greater than 100 ppm, and most preferably not greater than 50 ppm, with respect to the total amount of the composition. In particular, when the composition is used for a closed type of refrigerating machine, a low moisture content is required from the standpoint of its effects on the thermal and hydrolytic stability and the electric insulating property of the oil.

[0196] Nor are there any particular restrictions on the total acid value of the refrigerating machine oil composition of the invention, but the total acid value is preferably not greater than 0.1 mgKOH/g, and more preferably not greater than 0.05 mgKOH/g, in order to prevent the corrosion of metal used in a refrigerating machine or piping. The term "total acid value" as used here means the value (mgKOH/g) measured according to JIS K 2501 "Petroleum Products and Lubricating Oils—Neutralization Value Testing Method."

[0197] Nor are there any particular restrictions on the ash content of the refrigerating machine oil composition of the invention, but in order to improve the thermal and hydrolytic stability of the refrigerating machine oil composition of the present invention and thereby reduce the generation of sludge and the like, it is preferably not greater than 100 ppm, and more preferably not greater than 50 ppm. In the present invention, the term "ash content" means the value (ppm) measured according to JIS K 2272 "Testing Method for Ash Content and Sulfuric Acid Ash Content in Crude Oils and Petroleum Products."

[0198] Refrigerant

Refrigerants that can be used in refrigerating machines that

employ the refrigerating machine oil composition of the present invention include HFC refrigerants, fluorine-containing ether refrigerants such as perfluoroether; fluorine-free ether refrigerants such as dimethyl ether; and natural refrigerants such as carbon dioxide, ammonia and hydrocarbons. These refrigerants can be used alone or in combinations of two or more types.

[0199] Examples of HFC refrigerants include C_1 to C_3 , and preferably C_1 or C_2 , hydrofluorocarbons. Specific examples include HFCs such as difluoromethane (HFC-32), trifluoromethane (HFC-23), pentafluoroethane (HFC-125), 1,1,2,2-tetrafluoroethane (HFC-134), 1,1,1,2-tetrafluoroethane (HFC-134a), 1,1,1-trifluoroethane (HFC-143a), 1,1-difluoroethane (HFC-152a), and mixtures of two or more of these HFCs. These refrigerants are suitably selected according to the intended use and the required performance, but favorable examples include HFC-32 alone; HFC-23 alone; HFC-134a alone; HFC-125 alone; a mixture of 60 to 80% by mass HFC-134a and 40 to 20 % by mass HFC-32; a mixture of 40 to 70 % by mass HFC-32 and 60 to 30 % by mass HFC-125; a mixture of 40 to 60 % by mass HFC-125 and 60 to 40 % by mass HFC-143a; a mixture of 60 % by mass HFC-134a, 30 % by mass HFC-32, and 10 % by mass HFC-125; a mixture of 40 to 70 % by mass HFC-134a, 15 to 35 % by mass HFC-32, and 5 to 40 % by mass HFC-125; and a mixture of 35 to 55 % by mass HFC-125, 1 to 15 % by mass HFC-134a, and 40 to 60 % by mass HFC-143a. More specific examples include a mixture of 70 % by mass HFC-134a and 30 % by mass HFC-32; a mixture of 60 % by mass HFC-32 and 40 % by mass HFC-125; a mixture of 50 % by mass HFC-32 and 50 % by mass HFC-125 (R410A);

a mixture of 45 % by mass HFC-32 and 55 % by mass HFC-125 (R410B); a mixture of 50 % by mass HFC-125 and 50 % by mass HFC-143a (R507C); a mixture of 30 % by mass HFC-32, 10 % by mass HFC-125, and 60 % by mass HFC-134a; a mixture of 23 % by mass HFC-32, 25 % by mass HFC-125, and 52 % by mass HFC-134a (R407C); a mixture of 25 % by mass HFC-32, 15 % by mass HFC-125, and 60% HFC-134a (R407E); and a mixture of 44 % by mass HFC-125, 4 % by mass HFC-134a, and 52 % by mass HFC-143a (R404A).

[0200] Examples of natural refrigerants include carbon dioxide, ammonia, and hydrocarbons. The hydrocarbon refrigerant referred to here is preferably one that is a gas at 25°C at 1 atm. More specifically, this is C₁ to C₅, and preferably C₁ to C₄, alkanes, cycloalkanes, and alkenes, and mixtures of these. Specific examples of such hydrocarbon refrigerants include methane, ethylene, ethane, propylene, propane, cyclopropane, butane, isobutane, cyclobutane, methylcyclopropane, and mixtures of two or more of these compounds. Of these, propane, butane, isobutane, and mixtures of these are preferred.

[0201] In a refrigerating machine, the refrigerating machine oil composition of the present invention is normally in the form of a refrigerating fluid composition mixed with one of the refrigerants described above. There are no particular restrictions on the mix ratio of the refrigerating oil and the refrigerant, but the amount of the refrigerating oil is from 1 to 500 weight parts, and more preferably 2 to 400 weight parts, per 100 weight parts of refrigerant.

[0202] Refrigerating Machine

The refrigerating machine oil composition of the invention strikes

a good balance between all its performance requirements, such as lubricity, refrigerant miscibility, low temperature fluidity, and stability, and can be used favorably heat pumps, refrigerating machines, and so forth having a reciprocating or rotary, and open, semi-closed, or closed compressor. In particular, when this composition is used in a refrigerating machine in which aluminum components are used, a high level of performance can be achieved in terms of both thermal/chemical stability and preventing the wear of the aluminum components. Specific examples of such refrigerating machines include automotive air conditioners, dehumidifiers, refrigerators, cold storage freezers, vending machines, showcases, cooling apparatus used in chemical plants and elsewhere, household air conditioners, large building air conditioner systems, and heat pumps used for supplying hot water. In particular, if the refrigerating machine oil composition of the present invention contains a mixture of the ester (A-1) and ester (A-2), the best performance will be extracted when it is used as a refrigerating oil for a package air conditioner. Furthermore, the refrigerating machine oil composition of the present invention can be used in all types of compressors, such as reciprocating, rotary, centrifugal, and other such types.

[0203] A refrigerant circulation system in which the refrigerating machine oil composition of the present invention can be used favorably is typically made up of a refrigerant compressor, a condenser, an expander, and an evaporator, which are connected in that order along the flow path, and if necessary a drier may also be provided along the flow path.

[0204] Examples of refrigerant compressors include a high-pressure vessel type of compressor in which a motor comprising a rotor and a stator, a rotating shaft fitted in the rotor, and a compressor component linked to the motor via this rotating shaft are housed in a closed vessel filled with a refrigerating oil, and high-pressure refrigerant gas discharged from the compressor component is collected in the closed vessel; and a low-pressure vessel type of compressor in which a motor comprising a rotor and a stator, a rotating shaft fitted in the rotor, and a compressor component linked to the motor via this rotating shaft are housed in a closed vessel filled with a refrigerating oil, and high-pressure refrigerant gas discharged from the compressor component is directly discharged out of the closed container.

[0205] An insulating film used as the electric insulating system material for the motor may be a crystalline plastic film with a glass transition point of 50°C or higher, specific examples of which include one or more types of insulating film selected from the group consisting of polyethylene terephthalate, polybutylene terephthalate, polyphenylene sulfide, polyether ether ketone, polyethylene naphthalate, polyamideimide, and polyimide, as well as composite films in which a resin layer with a high glass transition point covers a film with a low glass transition point. These are preferred because of their resistance to deterioration in tensile strength and electric insulating property. The magnet wire which is used for the motor is preferably one with an enamel coating having a glass transition point of 120°C or higher, such as a single layer of polyester, polyester imide, polyamide, or polyamideimide, or an enamel coating which is a composite coating of

an upper layer with a high glass transition point over a lower layer with a low glass transition point. Examples of composite coating enamel wires include those in which a polyamideimide upper layer covers a polyester imide lower layer (AI/EI), and those in which a polyamideimide upper layer covers a polyester lower layer (AI/PE).

[0206] The drying agent packed in the drier is preferably a synthetic zeolite composed of an alkali metal silicate/aluminate compound salt with a carbon dioxide gas absorption volume of not greater than 1.0% at a pore size of 3.3 Angstroms or smaller and a carbon dioxide gas partial pressure of 250mmHg at 25°C. Specific examples include XH-9, XH-10, XH-11, and XH-600, which are trade names of Union Showa Co., Ltd..

Examples

[0207] The present invention will now be described in more specific terms by way of examples and comparative examples, but the invention is in no way limited to or by these examples.

[0208] Examples 1 to 16 and Comparative Examples 1 to 14

Refrigerating oil compositions having the components shown in Tables 1 to 6 were prepared using the base oils and additives listed below, for Examples 1 to 16 and Comparative Examples 1 to 14.

Base Oils

Base oil 1: tetraester of pentaerythritol and an equimolar mixture (100% branched chain type of fatty acid) of 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid (kinetic viscosity at 40°C: 68.5 mm²/s, pour point: -25°C, temperature of separation from R410A: 10°C)

Base oil 2: tetraester of pentaerythritol, heptanoic acid and a

mixture (linear fatty acid / branched fatty acid = 65/35) of pentanoic acid and 3,5,5-trimethylhexanoic acid (kinetic viscosity at 40°C: 56.5 mm²/s, pour point: -25°C, temperature of separation from R410A: 1°C)

Additives

- 5 Additive 1: tricresyl phosphate
- Additive 2: triphenyl phosphorothionate
- Additive 3: glycidyl-2,2'-dimethyl octanoate
- Additive 4: vinylcyclohexene dioxide
- Additive 5: phenylglycidyl ether
- 10 Additive 6: butyl stearate
- Additive 7: octylglyceryl ether
- Additive 8: diisodecyl adipate
- Additive 9: myristyl alcohol
- Additive 10: lauric acid

15 [0209] Next, the following tests were carried out to evaluate the refrigerating oil compositions of Examples 1 to 16 and Comparative Examples 1 to 14.

[0210] Stability Evaluation

20 A sealed glass tube test was carried out as set forth in JIS K 2211, using iron, copper, and aluminum as catalysts, and the sample was held at 200°C for 2 weeks and then checked to see if there was any sludge and if the catalyst had changed. The results thus obtained are given in Tables 1 to 6. In the column labeled "Sludge" in the tables, A means that no sludge was noted, and B that sludge was noted. In the column labeled

25 "Catalyst change," A means that there was no change, B that the catalyst changed slightly, and C that the catalyst changed markedly.

[0211] Evaluation of Anti-wear property and Friction property

The sliding component of a Falex tester (ASTM D2714) was placed in a pressure-resistant vessel, a refrigerant was introduced into the vessel, and a Falex test was carried out under the following conditions.

- 5 Test materials: steel ring, steel block
- Test starting temperature: 80°C
- Test duration: 1 hour
- Sliding rate: 0.5 m/s
- Load: 1250 N
- 10 Pressure of refrigerant atmosphere: 500 kPa

[0212] In the above test, the amount of wear was found as the weight change (reduction) in the block before and after the test, and anti-wear property was evaluated from this result. The frictional force was measured once every second, the resulting frictional force was divided
15 by the load, and the average coefficient of friction thus obtained was used to evaluate the friction property. The results thus obtained are given in Tables 1 to 6.

[0213] Hydrolytic Stability Evaluation

- 20 50 g of refrigerating oil composition whose moisture content had been adjusted to 500 ppm and 15g of catalyst were put in a 200 mL autoclave and held at 175°C for 2 weeks, after which the acid value (mgKOH/g) was measured. The results thus obtained are given in Tables 1 to 6.

[0214] Table 1

		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
Composition (% mass) by	Base oil 1	99.7	98.5	97.0	—	—	—
	Base oil 2	—	—	—	99.7	98.5	97.0
	Additive 1	0.1	0.5	1.0	0.1	0.5	1.0
	Additive 2	0.1	0.5	1.0	0.1	0.5	1.0
	Additive 3	0.1	0.5	1.0	0.1	0.5	1.0
	Additive 4	—	—	—	—	—	—
	Additive 5	—	—	—	—	—	—
	Additive 6	—	—	—	—	—	—
	Additive 7	—	—	—	—	—	—
	Additive 8	—	—	—	—	—	—
	Additive 9	—	—	—	—	—	—
	Additive 10	—	—	—	—	—	—
Stability	Sludge	A	A	A	A	A	A
	Catalyst change	A	A	A	A	A	A
Anti-wear property	Amount of wear (mg)	8.1	6.2	8.2	7.5	5.8	7.3
Friction property	Average coefficient of friction	0.130	0.127	0.128	0.129	0.126	0.127
Hydrolytic stability	Acid value (mgKOH/g)	0.02	0.04	0.06	0.11	0.14	0.15

[0215] Table 2

		Example 7	Example 8	Example 9	Example 10	Example 11
Composition (% by mass)	Base oil 1	99.2	98.0	96.5	99.2	98.0
	Base oil 2	—	—	—	—	—
	Additive 1	0.1	0.5	1.0	0.1	0.5
	Additive 2	0.1	0.5	1.0	0.1	0.5
	Additive 3	0.1	0.5	1.0	0.1	0.5
	Additive 4	—	—	—	—	—
	Additive 5	—	—	—	—	—
	Additive 6	0.5	—	—	—	—
	Additive 7	—	0.5	—	—	—
	Additive 8	—	—	0.5	—	—
	Additive 9	—	—	—	0.5	—
	Additive 10	—	—	—	—	0.5
Stability	Sludge	A	A	A	A	A
	Catalyst change	A	A	A	A	A
Anti-wear property	Amount of wear (mg)	6.0	6.0	6.1	6.2	6.2
Friction property	Average coefficient of friction	0.115	0.116	0.120	0.122	0.125
Hydrolytic stability	Acid value (mgKOH/g)	0.04	0.04	0.05	0.06	0.08

[0216] Table 3

		Example 12	Example 13	Example 14	Example 15	Example 16
Composition (% by mass)	Base oil 1	—	—	—	—	—
	Base oil 2	99.2	98.0	96.5	99.2	98.0
	Additive 1	0.1	0.5	1.0	0.1	0.5
	Additive 2	0.1	0.5	1.0	0.1	0.5
	Additive 3	0.1	0.5	1.0	0.1	0.5
	Additive 4	—	—	—	—	—
	Additive 5	—	—	—	—	—
	Additive 6	0.5	—	—	—	—
	Additive 7	—	0.5	—	—	—
	Additive 8	—	—	0.5	—	—
	Additive 9	—	—	—	0.5	—
	Additive 10	—	—	—	—	0.5
Stability	Sludge	A	A	A	A	A
	Catalyst change	A	A	A	A	A
Anti-wear property	Amount of wear (mg)	5.2	5.6	5.7	5.6	5.7
Friction property	Average coefficient of friction	0.110	0.112	0.120	0.121	0.124
Hydrolytic stability	Acid value (mgKOH/g)	0.14	0.14	0.15	0.16	0.18

[0217] Table 4

		Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6
Composition (% by mass)	Base oil 1	99.5	99.5	99.5	99.0	99.0	99.0
	Base oil 2	—	—	—	—	—	—
	Additive 1	0.5	—	—	0.5	0.5	—
	Additive 2	—	0.5	—	0.5	—	0.5
	Additive 3	—	—	0.5	—	0.5	0.5
	Additive 4	—	—	—	—	—	—
	Additive 5	—	—	—	—	—	—
	Additive 6	—	—	—	—	—	—
	Additive 7	—	—	—	—	—	—
	Additive 8	—	—	—	—	—	—
	Additive 9	—	—	—	—	—	—
	Additive 10	—	—	—	—	—	—
Stability	Sludge	A	B	A	B	A	A
	Catalyst change	A	C	A	C	A	B
Anti-wear property	Amount of wear (mg)	14.2	13.8	14.5	9.2	13.8	13.5
Friction property	Average coefficient of friction	0.145	0.135	0.130	0.143	0.138	0.133
Hydrolytic stability	Acid value (mgKOH/g)	0.21	0.25	0.01	0.28	0.02	0.04

[0218] Table 5

		Comp. Ex. 7	Comp. Ex. 8	Comp. Ex. 9	Comp. Ex. 10	Comp. Ex. 11	Comp. Ex. 12
Composition (% by mass)	Base oil 1	—	—	—	—	—	—
	Base oil 2	99.5	99.5	99.5	99.0	99.0	99.0
	Additive 1	0.5	—	—	0.5	0.5	—
	Additive 2	—	0.5	—	0.5	—	0.5
	Additive 3	—	—	0.5	—	0.5	0.5
	Additive 4	—	—	—	—	—	—
	Additive 5	—	—	—	—	—	—
	Additive 6	—	—	—	—	—	—
	Additive 7	—	—	—	—	—	—
	Additive 8	—	—	—	—	—	—
	Additive 9	—	—	—	—	—	—
	Additive 10	—	—	—	—	—	—
Stability	Sludge	B	B	A	B	A	A
	Catalyst change	A	C	A	C	A	A
Anti-wear property	Amount of wear (mg)	12.8	13.1	13.9	9.0	12.4	12.5
Friction property	Average coefficient of friction	0.142	0.132	0.127	0.141	0.136	0.132
Hydrolytic stability	Acid value (mgKOH/g)	0.33	0.36	0.08	0.38	0.11	0.12

[0219] Table 6

		Comp. Ex. 13	Comp. Ex. 14
Composition (% by mass)	Base oil 1	98.5	—
	Base oil 2	—	98.5
	Additive 1	0.5	0.5
	Additive 2	0.5	0.5
	Additive 3	—	—
	Additive 4	0.5	—
	Additive 5	—	0.5
	Additive 6	—	—
	Additive 7	—	—
	Additive 8	—	—
	Additive 9	—	—
	Additive 10	—	—
Stability	Sludge	A	A
	Catalyst change	B	C
Anti-wear property	Amount of wear (mg)	8.8	8.1
Friction property	Average coefficient of friction	0.144	0.141
Hydrolytic stability	Acid value (mgKOH/g)	0.21	0.25

[0220] Examples 17 to 20, Comparative Examples 15 to 24

In Examples 17 to 20 and Comparative Examples 15 to 24,
5 refrigerating oil compositions having the components shown in Tables 7
to 9 were prepared using the base oils and additives listed below.

Base Oils

A1: tetraester of pentaerythritol and an equimolar mixture of
2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid (kinetic viscosity
10 at 40°C: 68.5 mm²/s, pour point: −25°C)

A2: tetraester of neopentyl glycol and 2-ethylhexanoic acid
(kinetic viscosity at 40°C: 7.8 mm²/s, pour point: −40°C or less)

X1: ester of pentaerythritol and normal pentanoic acid (kinetic
viscosity at 40°C: 15 mm²/s, pour point: −40°C or less)

15 X2: diester of neopentyl glycol and oleic acid (kinetic viscosity at

40°C: 24 mm²/s, pour point: -40°C or less

Additives

B1: triphenyl phosphorothionate

C1: tricresyl phosphate

5 D1: glycidyl-2,2'-dimethyl octanoate

G1: vinylcyclohexene dioxide

G2: phenylglycidyl ether

10 [0221] Next, the following tests were carried out to evaluate the refrigerating oil compositions of Examples 17 to 20 and Comparative Examples 15 to 24.

[0222] Stability Test (1): SGT Test

15 A sealed glass tube test was carried out as set forth in JIS K 2211, using iron, copper, and aluminum as catalysts, and the sample was held at 200°C for 1 week and then checked to see if there was any sludge and how the catalyst looked. R410A was used for the refrigerant. The results thus obtained are given in Tables 7 to 9. In the column labeled "Sludge" in Tables 7 to 9, A means that no sludge was noted, and B that sludge was noted. In the column labeled "Catalyst change" in Tables 7 to 9, A means that no change was seen in the catalyst, B that a slight catalyst change was noted, and C that the catalyst appearance changed markedly.

20 [0223] Stability Test (2): Autoclave Test

25 50 g of refrigerating oil composition whose moisture content had been adjusted to 500 ppm was put in a 200 mL autoclave, the air in the system was completely removed with a vacuum pump, and then the system was returned to one-half (380 mmHg) normal pressure (760

mmHg) with air, 15 g of catalyst was charged into the system, and the temperature was held at 175°C for 2 weeks, after which the acid value (mgKOH/g) was measured. In this evaluation, the acid value of Comparative Example 15 was used as a reference, a grade of "A" was give if the acid value was less than the acid value of Comparative Example 15, and "B" if the acid value was less than the acid value of Comparative Example 15. The results thus obtained are given in Tables 7 to 9.

[0224] Evaluation of Anti-wear property

A Falex test (ASTM D2670) was carried out under the following conditions while a refrigerant was blown into a refrigerating oil composition. The amount of wear of the block and pin here was found as the reduction in weight of these components. The results thus obtained are given in Tables 7 to 9.

Test starting temperature: 25°C

Test duration: ~30 minutes

Load: 1000 N

Amount of refrigerant blown in: 10 L/hour

Refrigerant: R407C

[0225] Evaluation of Friction property

The sliding component of a Falex tester (ASTM D2714) was placed in a pressure-resistant vessel, a refrigerant was introduced into the vessel, and a Falex test was carried out under the following conditions. Friction property were evaluated from the average coefficient of friction. The average coefficient of friction was found by measuring the frictional force once every second, and dividing the resulting frictional force by the

load. The results thus obtained are given in Tables 7 to 9.

Test materials: steel ring, steel block

Test starting temperature: 80°C

Test duration: 1 hour

5 Sliding rate: 0.5 m/s

Load: 1250 N

Pressure of refrigerant atmosphere: 500 kPa

[0226] Evaluation of Oil Return Characteristics

10 A view window was provided in the compressor of a household
air conditioner (model PLZ-RP40A, made by Mitsubishi Electric; rated
cooling capacity of 3.6 kW), the height difference between the indoor
unit and outdoor unit was 20 meters, and the outdoor unit was installed
above the indoor unit so as to make the difference in oil return
characteristics more apparent. Various refrigerating oil compositions
15 were introduced into the compressor of this air conditioner, and first the
oil level was measured in a stationary state. Then, the operation of the
air conditioner was commenced, and how long it took for the oil level to
be restored to its original height (restoration time) was measured. The
results thus obtained are given in Tables 7 to 9. In the tables, the shorter
20 the restoration time, the better the oil return characteristics.

[0227] Table 7

		Example 17	Example 18	Example 19	Example 20
Composition (% by mass)	A1	69.98	69.79	68.95	67.90
	A2	29.99	29.91	29.55	29.10
	B1	0.01	0.10	0.50	1.00
	C1	0.01	0.10	0.50	1.00
	D1	0.01	0.10	0.50	1.00
Kinematic viscosity at 40°C (mm ² /s)		32.5	32.4	32.2	32.0
Stability (1) (SGT)	sludge	A	A	A	A
	catalyst change	A	A	A	A
Stability (2) (autoclave)	acid value	A	A	A	A
Anti-wear property	Amount of wear (mg)	10.2	9.8	7.9	7.7
Friction property	Coefficient of friction	0.125	0.122	0.120	0.118
Oil return characteristics	Restoration time (seconds)	785	785	780	785

[0228] Table 8

		Comp. Ex. 15	Comp. Ex. 16	Comp. Ex. 17	Comp. Ex. 18	Comp. Ex. 19	Comp. Ex. 20
Composition (% by mass)	A1	70.00	69.30	69.30	69.30	60.00	59.10
	A2	30.00	29.70	29.70	29.70	—	—
	X1	—	—	—	—	40.00	39.40
	B1	—	0.50	—	0.50	—	0.50
	C1	—	0.50	0.50	—	—	0.50
	D1	—	—	0.50	0.50	—	0.50
Kinematic viscosity at 40°C (mm ² /s)		32.5	32.4	32.3	32.3	34.2	33.6
Stability (1) (SGT)	sludge	B	B	A	B	B	A
	catalyst change	C	C	A	C	C	A
Stability (2) (autoclave)	acid value	B	B	B	A	B	B
Anti-wear property	Amount of wear (mg)	12.8	8.5	9.2	9.5	13.2	8.2
Friction property	Coefficient of friction	0.138	0.141	0.124	0.122	0.141	0.131
Oil return characteristics	Restoration time (seconds)	790	785	785	790	890	880

[0229] Table 9

		Comp. Ex. 21	Comp. Ex. 22	Comp. Ex. 23	Comp. Ex. 24
Composition (% by mass)	A1	68.95	68.95	—	—
	A2	29.55	29.55	—	—
	X1	—	—	—	—
	X2	—	—	100	98.50
	B1	0.50	0.50	—	0.50
	C1	0.50	0.50	—	0.50
	D1	—	—	—	0.50
	G1	0.50	—	—	—
	G2	—	0.50	—	—
	Kinematic viscosity at 40°C (mm ² /s)	31.9	32.1	24.0	23.9
Stability (1) (SGT)	sludge	B	B	B	A
	catalyst change	C	C	C	A
Stability (2) (autoclave)	acid value	B	B	B	B
Anti-wear property	Amount of wear (mg)	8.5	8.3	15.2	13.1
Friction property	Coefficient of friction	0.131	0.129	0.145	0.132
Oil return characteristics	Restoration time (seconds)	790	785	770	775